

## Experiment 4: Analysis of an Acid-Base Titration Curve - the Gran Plot

(Adapted from Daniel C. Harris' *Quantitative Chemical Analysis*.)

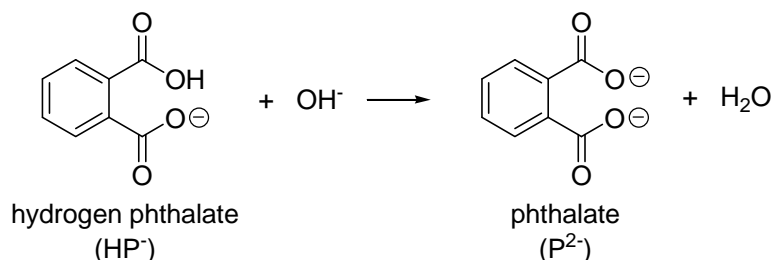
**90 minutes of experimental work, on your own (starting April 2)**

***You must make your measurements by April 15***

**Notebook Due on Friday, April 24** (by 4:00 pm  $\Rightarrow$  20% late penalty each 24 hour period thereafter)

### INTRODUCTION

In this experiment, you will titrate a sample of pure potassium hydrogen phthalate (KHP: See Harris Table 11-5) 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 Chemistry 111, 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 11-5). 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, we will have dried vials of potassium hydrogen phthalate for you, keeping them at 105°C for a long time. You will perform the titration using the Chemistry Department's Mettler DL12 Titrator. The titrator will be filled with an aqueous sodium hydroxide solution, which, when analyzed around April 1, was found to be very nearly 0.100 M. The actual concentration determined for it will be written on the board in the lab where the titrator is set up.**

In your notebook, you do **not** need to write down in detail how you operated the titrator. Do, however, write down brief descriptions of what you accomplished with it, record your pH data, make other specific observations and comments as asked for in this procedure, and follow good, standard notebook mechanics (table of contents, date, page numbers, introduction, etc.). Also, please tape in a copy of each of the graphs, and the spreadsheet, onto a separate page of your notebook, and e-mail a copy of the spreadsheet to me.

*Important note:* In acid-base chemistry it is important that the DI water you use is "fresh" from the DI water tap, not having sat around long enough to be acidified by absorbing carbon dioxide from the air. Don't use any water that's been in a squirt bottle for a long time!

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

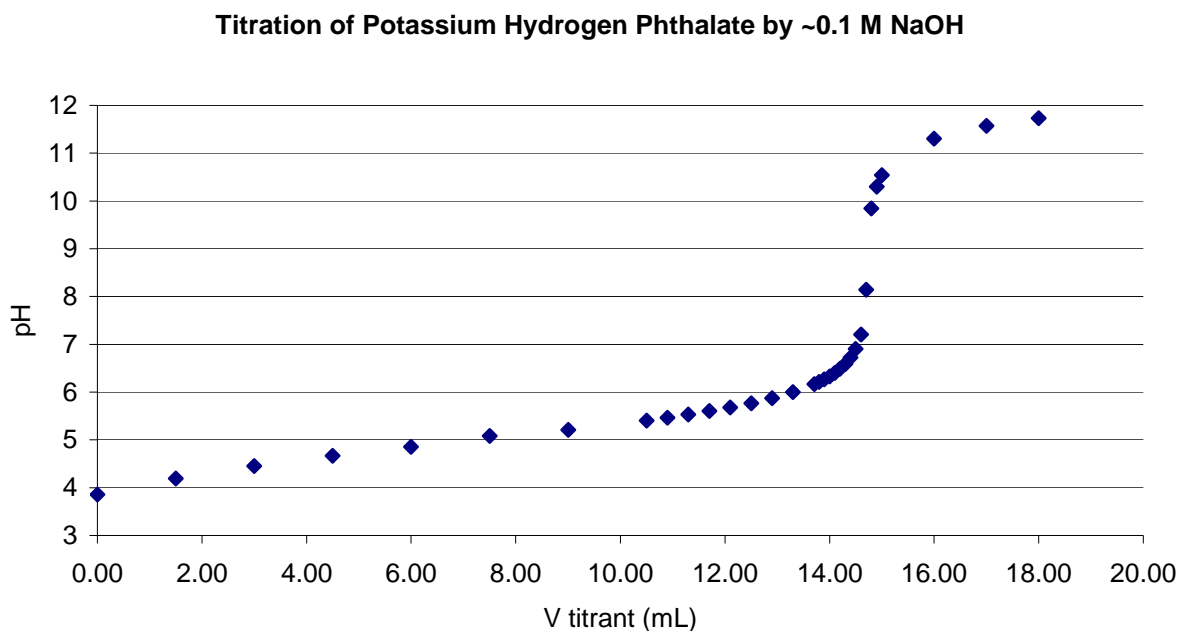


- e. Press the green START button at the lower right of the control panel. If all goes well, after a few seconds, you'll hear three beeps, confirming that the calibration was a success! Remove the sample cup containing the pH 10 buffer and rinse the electrode, buret tip, and stirrer as before.
3. Take a weighing bottle of potassium hydrogen phthalate from the desiccator, along with a lid.
4. Using an analytical balance, weigh out close to 0.3 g of the potassium hydrogen phthalate (KHP), and transfer it into a 50-mL volumetric flask. The mass need not be exactly 0.3000 g, but the mass *actually transferred into the volumetric flask* should be recorded to 4 significant figures.
5. Add some DI water to the flask and completely dissolve the solute. Be patient--KHP is rather slow to dissolve. Once it has completely dissolved, dilute to the mark with more DI water.
6. Pour the 50 mL of KHP solution into a clean, dry sample cup. Rinse out the volumetric flask twice with a little water. (Why do this? Why use only a little water? Please comment.)
7. Add two drops of phenolphthalein indicator to the contents of the sample cup! Don't forget this!
8. Mount the sample cup onto the titration head, and then press the STIR button (in the second column from the left on the control panel). Verify that the stirrer is doing its thing.
9. Now take a few moments to calculate a theoretical equivalence point based on the reported  $[\text{OH}^-]$  and the mass of KHP (FW 204.22). (Obviously, you should do this in your notebook and not on some random scrap of paper...*please* let that be obvious!?!)
10. Press the MAN 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.)
11. 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 MAN 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.
12. Press the mL pH button. Then press and hold down the MAN 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. (If you miss a target volume by a little bit, no sweat – you're just collecting points for a plot.)
13. 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.
14. 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).
15. At 1 mL before the equivalence point, you should start adding base only 0.01 mL at a time. However, you only need to record the pH every 0.10 mL. (You may need to wait longer than 15 s for the pH reading to stabilize.) The reason you are adding base so slowly is that you want to determine (and write down) the volume at which the very first faint pink color persists. [You might be better able to see it if you hold a white surface behind the sample cup.] Once the phenolphthalein end point is reached, add three more 0.10-mL aliquots, recording the pH each time (after waiting 15 s). In your notebook, record how stable the pH readings are at this point, and briefly explain your observation.
16. 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).
17. When you have collected all your data, press RESET. Remove the sample cup, and rinse the buret tip, stirrer, and electrode thoroughly, as before. Pour the cup contents into the sink, rinse it several times with DI water, and dry. (Do not use any soap on it!) Leave the cup next to the titrator.

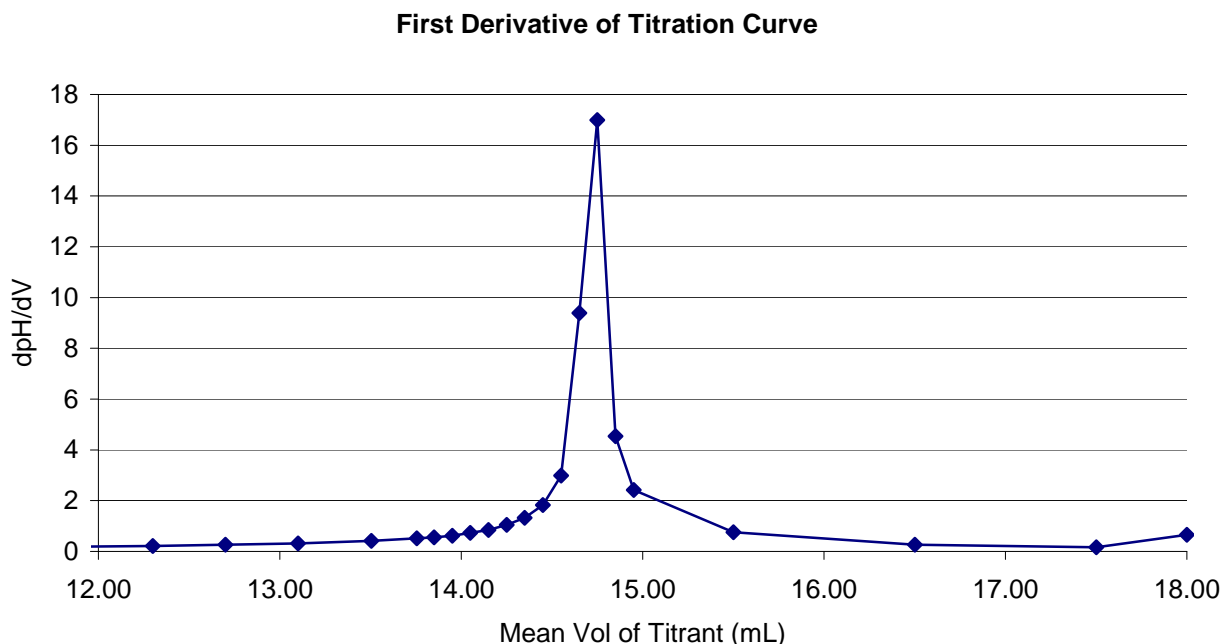
- Carefully remove the electrode from the titration head and return the electrode to its storage sleeve. Don't attempt to dry it first; it's fine to stick it in there with DI water on it.
- Clean up the rest of your glassware (leftover KHP can go down the sink). Leave the titrator on.

## DATA ANALYSIS

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

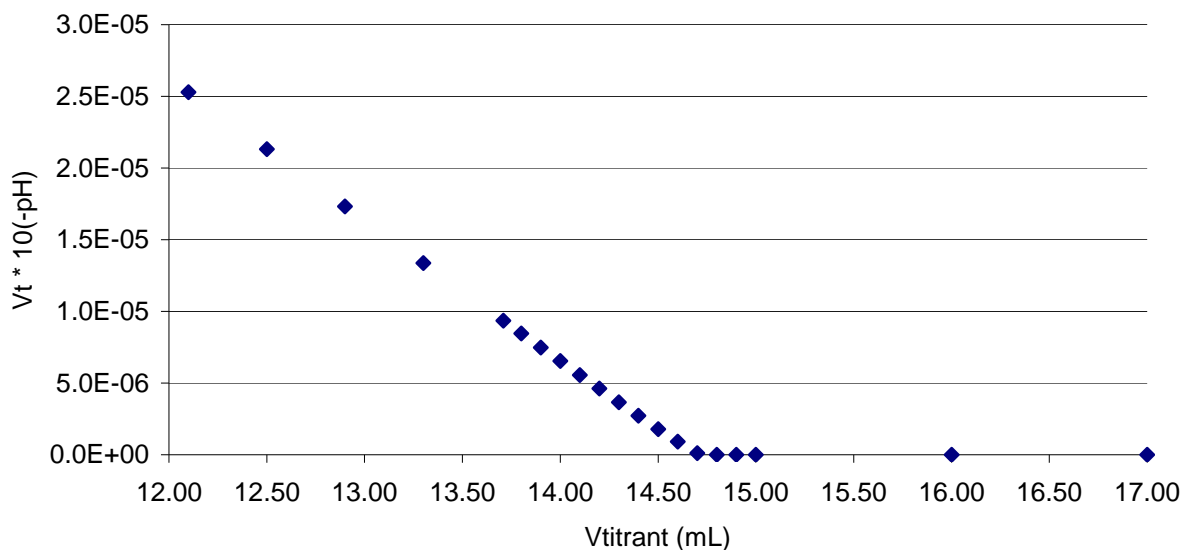


- Report your titration endpoints as determined by (a) the indicator and (b) a first derivative plot (see pp. 210 - 211 of your text). Your notebook should include a plot like this:



- Although the KHP was the “analyte” in your titration, it is actually used to standardize (that is, determine the concentration of) the  $\text{OH}^-$  solution. Use your phenolphthalein and first derivative endpoints to calculate two estimates of the concentration of  $[\text{OH}^-]$  in the titrant.
- Construct a Gran plot ( $V_{\text{titrant}}10^{-\text{pH}}$  vs.  $V_{\text{titrant}}$ ). Plot for  $V_{\text{titrant}}$  ranging from  $\sim 0.8V_e$  to past  $V_e$ . Use your first derivative endpoint as your  $V_e$  value. Tape a copy of a plot like this into your notebook:

**Preliminary Gran Plot for Titration--0.8  $V_e$  to past  $V_e$**

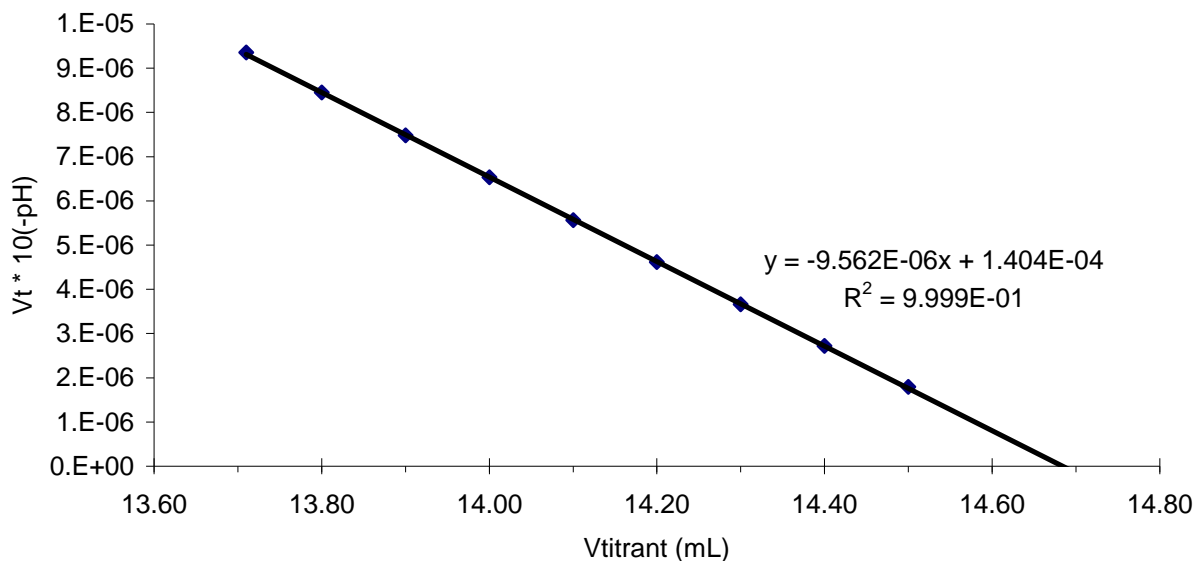


(The plot becomes non-linear when  $V_{\text{titrant}}$  is very close to  $V_e$ . This is largely due to the breakdown of our assumption that  $\text{mol P}^{2-} = \text{mol OH}^-$  added. This assumption starts to fail because  $[\text{HP}^-]$  is quite low close to the endpoint. Hence, the reverse of the titration reaction,  $\text{P}^{2-} + \text{H}_2\text{O} \rightarrow \text{HP}^- + \text{OH}^-$ , becomes non-negligible, as predicted by Le Chatelier's Principle.)

- 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 before  $V_e$ . Then add a trendline to these data. You can do this in Excel as follows:
  - Select “Add Trendline...” from the Chart pull-down menu.
  - On the “Type” tab, choose a linear Trend/Regression Type.
  - On the “Options” tab, choose to display both the equation and R-squared value on the chart. Also choose to forecast forward by 1 unit. (You want your plot to display the x-intercept.)
  - Hit OK and marvel at what you have wrought. Behold, lo, but it is lovely, is it not?
  - Click once on the equation of your trendline and then select Format: Selected Data Labels... from the top menu. On the Number tab, choose scientific and display 3 decimal places.

The statistical parameter  $R^2$  is the (often misused) correlation coefficient. While it can not tell you if you have a *good* fit, it can tell you whether a line fits a set of points better than some other line, or whether one set of points or another is better fit by a line. You'll be using it for the latter, here, realizing that points that fall perfectly on a 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 (Professor Kuwata chose to include his data between 13.70 and 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  $\text{OH}^-$  concentration based on the Gran plot value for  $V_e$ .

6. Find the average and 95% confidence interval for your three  $[\text{OH}^-]$  values (phenolphthalein, first derivative plot, and Gran plot). Using a Case 1  $t$ -test, determine if there is a statistically significant difference between the average of your three measurements and the formal  $\text{OH}^-$  concentration we put up on the board. If there is, offer a possible reason for the discrepancy.
7. Finally, use the slope of your final Gran plot (equal to  $-\frac{\gamma_{\text{HP}^-}}{\gamma_{\text{P}^{2-}}} K_a$ ) 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 match what's on your chart.)
  - b. Next, compute the total ionic strength of the solution close to the endpoint. Clearly,  $\mu$  is increasing throughout the titration. We will choose arbitrarily to compute  $\mu$  at around the midway point of our final Gran plot:  $0.95V_e$ , where we use the  $V_e$  determined from the Gran plot. Consider the contributions of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{HP}^-$  and  $\text{P}^{2-}$ . (The value of  $[\text{Na}^+]$  will be equal to the concentration of the NaOH solution given in class.)
  - c. Next, determine activity coefficients [at the ionic strength determined in (b)] for  $\text{HP}^-$  and  $\text{P}^{2-}$ , assuming that both ions have a hydrated radius  $\alpha = 600$  pm. 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  $K_a$ . (Assume that uncertainties in the activity coefficients of  $\text{HP}^-$  and  $\text{P}^{2-}$  are zero.)

Please tape a copy of your spreadsheet into your notebook, and e-mail me a copy as well. End your notebook entry with a conclusion, in which you assess the various means of determining the endpoint, relative to each other, as well as comment on where the greatest uncertainty in your  $K_a$  value likely arises. (Identify what you think are the **one or two most important sources** of error!)