

Great Hungers feed themselves,  
but little Hungers ail in vain.  
--Emily Dickinson

## A Closer Look at Acid-Base Neutralization Reactions

The quantitative relationship between two reacting *solutions* is very important to a chemist. In reactions involving precipitates or gas formation we have already seen ways in which to quantify the chemical process through a description involving the use of stoichiometry. In acid-base, or neutralization reactions often neither of these two results occur. It is therefore important to have a method which will allow quantification of results. Titration is a method of adding a known concentration and volume of acid or base to an unknown concentration of acid or base. The point at which equal amounts of  $\text{H}_3\text{O}^+$  (or  $\text{H}^+$ ) and  $\text{OH}^-$  ions have been added is usually determined with a chemical that changes color (an "indicator") or some type of instrumentation. You have used indicators in previous experiments to detect the "endpoint" of a neutralization reaction.

In this experiment you will investigate the behavior of acids and bases in neutralization reactions by two different titration methods. You are already familiar with the traditional approach, using an indicator to signal the endpoint. Now you will investigate some properties of the reacting acid/base mixture using two instrumental techniques: pH and conductometric titration.

The second part of the experiment involves determining the molar mass of an unknown solid acid using either of the two instrumental methods previously investigated. In titration of acids and bases it is the *moles* of  $\text{H}_3\text{O}^+$  (or  $\text{H}^+$ ) and  $\text{OH}^-$  that are equal at the equivalence point\* and therefore it is possible to determine the moles of an unknown sample if a base or acid of known concentration is used to titrate it. Once the moles of sample are known it is a simple matter to relate these to the sample mass and determine the molar mass [you may want to take a look back at **The Carbonate Project** to review some of these ideas].

\*the equivalence point is the actual stoichiometric ratio which yields a complete reaction between acid and base; the "end-point" is when the indicator changes color--ideally, they are the same.

## Preparing to experiment

You will be provided with the following materials:

1. 0.10 M HCl solution (use 10.0 mL)
2. an unknown concentration of NaOH solution
3. a solid unknown acid (use about 0.25 g in about 40 mL distilled water)
4. a 10 mL volumetric pipet
5. a pipet filler
6. a magnetic stirrer and stirring bar
7. a pH electrode
8. a conductivity probe
9. a buret and clamp

Design an experiment to determine the concentration of the unknown sodium hydroxide solution using the standard 0.10 M HCl by following the progress of the reaction with a pH electrode and conductivity probe.

Design an experiment to determine the molar mass of the solid acid unknown using the sodium hydroxide solution and the pH electrode method from your previous titration.

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**BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.**

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Equipment



volumetric pipet

### Pre-lab take-home quiz

These questions should be answered on a separate sheet of paper to be turned in on the day you begin this experiment.

1. 15.0 mL of 0.15 M HCl was titrated with 17.9 mL of NaOH. What is the concentration of the NaOH in moles/Litre?
2. A sample of *impure* NaOH with a mass of 0.764 g required 116 mL of 0.075 M H<sub>2</sub>SO<sub>4</sub> for neutralization. What was the % by mass of NaOH in the sample? [*hint*: the molar ratio of reaction between NaOH and H<sub>2</sub>SO<sub>4</sub> is not 1:1]
3. If you wanted to do an instrumental titration without *first* doing a traditional titration by indicator, how might you estimate the equivalence point so that you would know when to stop?

### Technique

#### 1. Semi-automatic titration

The CBL cannot add base for you and complete a titration on its own, but it can record data about your reaction at intervals. More sophisticated devices actually use precision pumps to deliver small volumes (fractions of mL) at regular intervals as data is recorded. In this exercise, it is convenient to simulate this type of device. Realistically speaking, it would be impractical to manually add NaOH in fractions of mL. The process would take too long. However, you can get reasonably good instrumental results with the solutions provided by adding base gradually so that at each addition the pH changes by about 0.2 units. Initially, this will take more base, but as you approach the equivalence point, less will be required. Past the equivalence point, more will again be needed. If the CBL is set up for the VS. USER X mode, you can record the pH and enter a volume of base for each addition from the buret.

The pH changes slowly at first, then very rapidly near the equivalence point, and then slows down again. Thus you can judge when the equivalence point has been passed. In order to produce data which will help you determine the equivalence point accurately, you should add a total of 2 additional mL of base *after* the equivalence point has been reached.

The conductivity titration is done in the same way, but the behavior of the solution is different. The conductivity changes gradually throughout the titration so it is generally sufficient to simply add the base in regular intervals (0.5 mL will work well) and record the conductivity after each addition. It is not possible (although desirable, in terms of time) to do both titrations simultaneously because the current generated by the conductivity probe interferes with the pH electrode. Individually, each titration can be followed graphically or digitally. There is an advantage to doing both graphically because you can see the sudden change near the equivalence point more clearly. For the graphical approach you should use the VS. USER X option with VOLUME (ML).

Typical parameters for the graph when measuring pH : Ymax = 14, Ymin = 0, Xmax = 20, Xmin = 0. **For the titration of the unknown Xmax should be set to 30.**

#### 2. pH electrodes

The pH electrode is stored in a salt solution and must never be allowed to dry out. It is also very fragile at the measuring end and is therefore protected with a little plastic "fence". Handle it with care. Remove the electrode from its storage solution by unscrewing the bottle cap [the cap remains attached]. Rinse the electrode with a stream of distilled water from your wash bottle and dry it gently with a kimwipe.

When you choose **pH** on the CBL, you will be asked what buffer solutions you will use to calibrate the electrode. For an experiment like this which covers a wide range of pH it is usual to use buffers of pH 4 and pH 10. The calibration sequence is similar to that used for the colorimeters. Just follow the screen directions carefully. ALWAYS press [ENTER] on the calculator when prompted to do so on the screen before pressing any buttons on the CBL. This ensures that the calculator is able to get the information it needs from the CBL when you press the [TRIGGER] button.

Once your electrode is calibrated, remove it from the buffer solution, rinse it carefully, dry it, and replace it in its storage solution while you complete your setup. Be sure to rinse it off again and dry it before placing it in your solution.

#### 3. Measuring conductivity

You have used a small semi-quantitative conductivity device in past experiments. But conductivity can also be strictly quantified. The probe you will use in this experiment is similar to the simple battery-operated one but it gets its power from the CBL.

**The conductivity probes are permanently attached to their amplifiers which have switches on the side for three different ranges. For this experiment the switch should be in the upper position (0-20000  $\mu$ S)**

Like the pH electrode, the conductivity probe is subject to the ravages of experimental handling and so must be calibrated each time it is used. Two standard solutions are provided for you to use. The calibration routine is similar to the others--you place the electrode in one solution and then after a press of the [TRIGGER] button the calculator asks for the "real" value---this would correspond to the conductance value given on the bottle of solution you use (this is the  $\gamma$  value on the label). Be sure to rinse and dry the electrodes between solutions just as you do with the pH electrode.

Equilibration of the conductivity electrode may take a little longer than the pH electrode so be sure to give it time to settle down before pressing [TRIGGER]. Best results are obtained if the solutions being measured are stirred constantly. Magnetic stirring bars are already in the bottles.

Unlike the pH electrode, the conductivity probe can be stored dry while you are not using it, but it works a little better with an initial soak so you will find it standing in a beaker of distilled water. Be sure to replace it there when you are finished with it.

The units of specific conductance displayed on the CBL (and sent to your calculator) are milliSiemens or mS. The symbol for specific conductance is the lower case Greek letter gamma,  $\gamma$ .

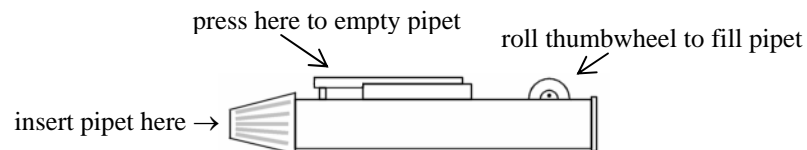
Typical parameters for the graph when measuring conductivity :  $Y_{\max} = 15$ ,  $Y_{\min} = 0$ ,  $X_{\max} = 20$ ,  $X_{\min} = 0$ .

#### 4. Pipets

You have used graduated cylinders in the past to measure volumes of solution. One step beyond the graduated cylinder in terms of precision is the *pipet*. A pipet looks like a large eye dropper without a bulb. There are two basic types of pipets. One is *volumetric*. This has ONE mark on it and is good for repeatedly measuring out a single volume. It comes in many sizes but each is good for only one volume. A *measuring* pipet, on the other hand, is very much like a graduated cylinder. It has many marks and also comes in many sizes, each of which covers a range of volumes. You will use 10 mL volumetric pipets in this experiment.

Like most pipets, these are graduated "To Deliver" (you might see the mark **TD** on the barrel somewhere) unlike graduated cylinders which are calibrated "To Contain". Thus they give more reproducible (more *precise*) volumes each time.

In the olden days pipets were filled by mouth. **THIS IS FORBIDDEN IN THE LAB!!!!!!** We are providing you with pipet fillers which attach to the pipets and allow you to fill and empty with relative ease:



Before using a pipet to measure with, it is good practice to draw up a little of the solution to be measured and rinse it around the walls of the pipet, then discard it.

#### 5. Sleeping calculators

Unlike the proverbial sleeping dogs, it is not a good idea to let your calculator sleep through the experiment. If you are taking a great deal of time adding your volumes of NaOH and waiting for a stable reading before pressing [TRIGGER] it is possible that your calculator could go to sleep. If that happens it is very important to wake it up (just press ON once) before pressing [TRIGGER]. Otherwise the program will halt and you will have to copy out the rest of the data by hand.

#### Analysis

**[note: titration data must be included with your report—see following page]**

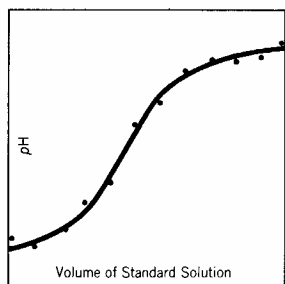
1. Use your data to determine the concentration of the NaOH solution. To do so you need to determine the volume of NaOH needed to reach the equivalence point. You must plot graphs of each measured quantity (pH and conductance) vs. mL NaOH. Once you know the volume of base added to reach the equivalence point, this can be compared with the volume and Molarity of acid used. Recall,  $V_a M_a = V_b M_b$  and NO, this is not the same thing as  $V_1 M_1 = V_2 M_2$ . "a" and "b" in the formula stand for "acid" and "base". [see following page]
2. Determine the "best" value for the concentration of the NaOH. Report how you arrived at this value and be sure to use it for the next calculation. "Best value", in this context, would typically be a simple average, but if your two values are very different you will need to pick one and defend it.
3. Use the determined concentration of the NaOH and the data from the solid acid titration (plot a graph!) to calculate the molar mass of the unknown solid acid. [all solid acids react with NaOH in a 1:1 ratio]
4. Identify your solid acid from the list given below:

$\text{KHSO}_4$	136.2 g/mol
$\text{KHC}_4\text{H}_2\text{O}_4$	154.1 g/mol
$\text{KHC}_8\text{H}_4\text{O}_4$	204.2 g/mol

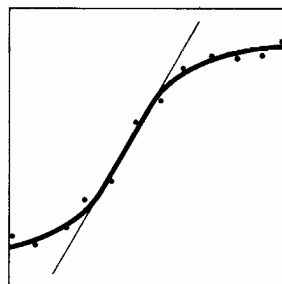
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## Interpreting pH titration curves

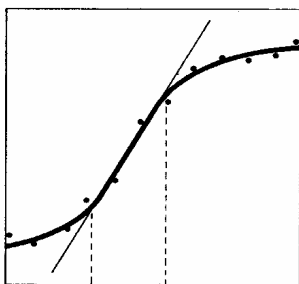
You will have noticed that the pH of the solution changes rapidly near the endpoint. In very careful work the base would be added drop-by-drop in this region and the pH noted after each drop. A graph of pH vs. mL of base added shows a characteristic "s" shape. It is possible to determine the endpoint of a titration from a carefully prepared curve. Consider the sequence of diagrams shown below:



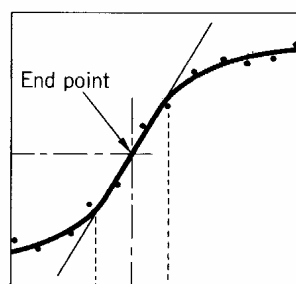
1. Draw smoothed curve through experimental points.



2. Draw steepest tangent.



3. Draw ordinates at points where tangent departs from the smoothed curve.



4. Draw end-point ordinate midway between the two ordinates of Step 3.

If you are very lucky and your equivalence point region is essentially vertical you may be able to use the average of the volume measurements just before and just after the equivalence point as the true equivalence point. The more careful your additions of base in the equivalence point region, the greater the likelihood this will be the case.

## Interpreting Conductance titration data

This is more straightforward than the pH data. As the added base reacts with the acid in the beaker, more and more water forms while hydronium and hydroxide ions are consumed. This makes the conductance of the solution drop (especially since added base is mostly water anyway). At the equivalence point, the conductance will be at a minimum (but not zero....why??).

### Dealing with all that data

Problem 1: how to print it all out

1. Go to the Science Resource Center and start the program *TI Connect*.
2. Select "Data Editor" (lower left) and click on the box at the bottom of that frame which says "Matrix"
3. Plug your calculator into the GraphLink cable at the computer (it should turn on automatically—if not, turn it on). Click on the second icon in the first row of the Data Editor screen (looks like a magnifying glass and a calculator).
4. If you have a good connection a directory of your calculator memory will appear. Data from the lab is always stored in matrix H (and I, if there is a lot). Click on the "+" next to "Matrix" in the listing for your calculator memory and then double-click on [H] to transfer the contents of the matrix to the Data Editor.
5. You can now print all of the data in the editor by using the Print icon. Individual sets of data (from each titration) are separated by a -2000 marker in the first column. If you like, you can delete all the data from the editor except what you want to print, or just print it all and then write on the sheet what each set is.

Of course, you can do all of this at home if you can find the Link cable that came with your *Silver Edition*, have a computer with a USB port AND have the *TI Connect* software (free) installed.

Problem 2: how to avoid typing all the data into Excel to graph it

1. If you have followed the directions above you can also save the data on the screen in a format that Excel can open. Then you can do what you want with it. From the File menu select Export. The default export format is called "CSV" (comma separated value) which Excel can open. Select the directory or disk where you want the file to go and click on "Save". Exit the *TI Connect* program.
2. When you start Excel and choose "Open" from the File menu first change to the directory or disk where you stored your CSV data file. Then go to the bottom of the box and change the "Files of type" to "All files".
3. Double click on your file (maybe H.CSV?) to open it and then do as you would normally to graph it. Remember, if you simply exported the entire matrix, the individual titrations are separated by a -2000 marker in the first column