Lab #3
Potentiometric Titration of Soda Ash
(after Christian, p.692-694, p.718-720)

I: INTRODUCTION

In this lab, an unknown sample of soda ash (a crude mixture of sodium carbonate) will be titrated with a standard 0.1 M HCl solution. Since $\text{CO}_3^{2-}$ is a diprotic base, there will be two endpoints, and two different indicators -

$$\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^- \quad \text{(phenolphthalein)}$$

$$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2 \quad \text{(methyl red)}$$

Note that between the first and second endpoint (as shown in Figure 1), a gradual decrease in pH occurs due to the presence of a naturally occurring HCO$_3^-$/CO$_2$ buffer system (produced from absorption of CO$_2$ from the atmosphere). This will give a poor visual endpoint, unless the buffer couple is destroyed. In practice, the visual titration used for standardization is continued until the methyl red endpoint is reached. At this time the solution is gently boiled to remove the CO$_2$, leaving only the remaining HCO$_3^-$ that is then titrated to completion.

![Figure 1](image-url)
II: PROCEDURE FOR STANDARDIZING 0.1 M HCl

Concentrated hydrochloric acid has a density of 1.18 and contains 37% by weight HCl. Therefore about 8 mL concentrated acid should be diluted to 1 L to make 0.1 M. Measure about 1 mL more than this amount into a 50 mL graduated cylinder and pour into a 1 L volumetric flask (obtain from stockroom) that is almost filled to 1000 mL with distilled water (ALWAYS ADD ACID TO WATER, not the other way around). Stir until thoroughly mixed. Store your solution in a 1-L glass bottle.

You will standardize your HCl against primary standard Na₂CO₃. Sodium carbonate is extremely hygroscopic! Dry about 1 gram in the oven at 160 °C for two hours or more. Cool for at least 20 minutes in a dessicator before weighing. Obtain a sample of your unknown and dry the same way.

Weigh accurately three 0.2 g samples of primary standard Na₂CO₃ into 250 mL Erlenmeyer flasks. Add about 50 mL of distilled water to each and one to two drops of phenolphthalein indicator.

Titrate the first sample of the sodium carbonate, adding the acid no faster than 0.5 mL per second, swirling the flask constantly until the pink color disappears. At this point, about half the total acid necessary has been added (actually a slight excess). Use this number to estimate where the final endpoint will occur, keeping in mind that slightly less acid should be required than has been added.

Add 2-4 drops of methyl red indicator. The color change for this indicator is from yellow to red (see Figure 1 again). The correct color for the second endpoint can be determined by comparison with the color of a few drops of the indicator in a solution of 0.20 g KHP in 100 mL of distilled water. Titrate to a point just before the endpoint as indicated by a transition color. Interrupt the titration at this point and boil the solution carefully for 2 to 3 minutes to drive off the carbon dioxide. The color should revert to yellow; continue the titration to the red endpoint color. This marks the final endpoint. If the color change is not sharp, repeat the heating to remove carbon dioxide.

Titrate the other two samples in the same manner as the first and calculate the molarity of the HCl from the weights of Na₂CO₃ taken, remembering that each carbonate reacted with two protons.
III: PROCEDURE FOR TITRATING THE UNKNOWN

1. **Trial Titration - NO BOILING.** The purpose of this titration is to locate quickly and approximately the two endpoints. Weigh accurately a 0.4 g sample of unknown soda ash and add it to a 400 mL beaker containing a magnetic stirring bar. Add approximately 50 mL of water and a few drops of phenolphthalein indicator (the solution will turn pink). While stirring, titrate with standard HCl to the first endpoint (the phenolphthalein color disappears). Write down the volume of the first endpoint. Now add a few drops of methyl red indicator (the solution turns yellow). Titrate until the second end point is reached (red color without a trace of intermediate orange color). Write down the second endpoint volume.

2. **Final Titration - WITH BOILING FOR THE SECOND ENDPOINT ONLY.** Weigh accurately another sample of the unknown and titrate as before, but after the second endpoint bring the solution to a gentle boil to drive off the CO₂. The solution color will shift back to yellow as the pH rises. Resume titrating until the color changes to red or pink.
PART IV: Calculating the Volume at the Endpoint using Microsoft Excel

We will identify the endpoint by calculating the second derivative numerically. The main idea to keep in mind is that a derivative is nothing more than the slope of the curve at a point (in other words, the derivative is a tangent line to a curve). Therefore we will approximate the derivative by calculating \((y_2-y_1)/(x_2-x_1)\) between successive points on the curve. The volume will be the average of \(x_2\) and \(x_1\). These ideas are illustrated in Figure 3.

![Figure 3](image)

NOTE: In the following directions, enter text between quotes at the indicated locations without the quotes!

1. Enter the following labels in the indicated cells:

   - A1: "mL"
   - B1: "pH"
   - C1: "mL"
   - D1: "1st Deriv"
   - E1: "mL"
   - F1: "2nd Deriv"
2. Enter your data in columns A and B starting in row 2. Plot the titration curve using the **Chart Wizard.** Make certain that you select an **XY (Scatter) Chart Type** and **Format 2** when plotting the data. These two Chart Wizard screens are shown in Figure 4. Refer to Lab #1 on Statistics to review graphing if you forgot how to do it. Your titration curve should appear similar to Figure 5.

![Figure 4](image1)

![Figure 5](image2)
3. Move the cursor to cell \( c3 \). Type in \( =\text{average}(A2:A3) \). Copy this formula down to the end of your column of data.

4. Move the cursor to cell \( d3 \). Type in the formula \( =(B3-B2)/(A3-A2) \). This will be the average slope between your first two data points. This slope is equal to the \textbf{1st derivative} for you non-calculus folks. Copy this formula down to the end of your data. The volume of titrant you calculated in step 3 corresponds to these slopes.

5. Move the cursor to cell \( e4 \). Enter \( =\text{average}(C3:C4) \) and copy down to the end of your data. These are the volumes of the \textbf{2nd derivative}.

6. Now you can calculate the second derivative by taking the derivative of the first derivative. Move the cursor to cell \( f4 \). Type in the formula \( =(D4-D3)/(C4-C3) \). Copy this formula down to the end of your data.

7. Create a second graph of your numerical second derivative using column E as the x-axis and column F as the y-axis. The second derivative will pass through zero at the endpoint. It's probably a little obscure with so many data points so we will have to zoom in on it. Write down your estimated volume at the endpoint before proceeding. Your graph will appear similar to Figure 6.

![Figure 6](image-url)
8. Increase the size of the 2nd derivative graph so that it fills up a significant portion of the screen. Double-click on the 2nd derivative graph to edit it; the graph will become surrounded by cross-hatching.

9. Double-click on the xaxis; the window shown in Figure 7 will appear. This box allows us to edit the patterns, scaling and other display features of the xaxis. Make sure that the Patterns tab has been clicked. Make sure that your options on this screen are the same as in the figure, e.g. Axis = automatic, etc.

![Figure 7](image)

10. Now click on the Scale tab. The window will appear as in Figure 8 on the next page. On the left-hand side of the window is a column of "check boxes" that currently have an x in them. Click on all of the x's to disable the auto selection. Enter in the Minimum and Maximum boxes values for the milliliters of titrant right before and after the 2nd derivative passes through zero. For example, I used values of 31.5 and 32.5 mL respectively (Figure 9).
11. Change the **Major Unit** value to "0.1" and the **Minor Unit** value to "0.01". Your graph should look similar to Figure 9 below. Notice how you can read the volume of titrant to the nearest 0.01 mL by reading directly off of the graph! Continue to zoom in using the **Minimum** and **Maximum** boxes until you can clearly see the volume.
12. Repeat this process for your other two titration curves. Calculate the percent purity of your unknown by using these volumes. Then calculate the percent purity based on the methyl red indicator.

13. Hand in the file card with the percent purity of your sample, and hand in a plot of your titration curve.