Chemistry 119: Experiment 5

Determination of Carbonate

Many analytes are weak acids or weak bases and can be titrated with a strong base or a strong acid, respectively, in order to observe a sharp, analytically useful endpoint. The most common acid titrant is HCl.

Carbonate ion is a weak base which can be titrated with an acid to two equivalence points:

1\textsuperscript{st} equivalence point: \[ \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^- \]  
(12.1)

2\textsuperscript{nd} equivalence point: \[ \text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^- \]  
(12.2)

HCl is a strong acid that reacts completely with the carbonate, i.e. the neutralization equilibrium lies far to the right –

\[ \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \rightleftharpoons \text{HCO}_3^- + \text{H}_2\text{O}. \]  
(12.3)

Before the titration begins, the sample is a weak base solution in which [OH\textsuperscript{-}] = [HCO\textsubscript{3}\textsuperscript{-}]. As H\textsuperscript{+} is added, more HCO\textsubscript{3}\textsuperscript{-} is formed. Since the sample contains substantial amounts of CO\textsubscript{3}\textsuperscript{2-} and HCO\textsubscript{3}\textsuperscript{-} at this point, it is a buffer solution (pH \sim pK\textsubscript{a2}). At the first equivalence point, all the carbonate has been converted to bicarbonate. The bicarbonate ion is amphiprotic, it is a weak base and a weak acid. The base strength of HCO\textsubscript{3}\textsuperscript{-} is higher than the acid strength (compare \textit{K}_b\textsubscript{2} to \textit{K}_a\textsubscript{2}) so the solution is basic. As more H\textsuperscript{+} is added, H\textsubscript{2}CO\textsubscript{3} is formed. As long as there are substantial amounts of HCO\textsubscript{3}\textsuperscript{-} and H\textsubscript{2}CO\textsubscript{3} in solution, it is a buffer that has a pH near pK\textsubscript{a1}. At the second equivalence point, all the bicarbonate has been converted to carbonic acid. Carbonic acid is a weak acid. The acetate ion is a weak base. H\textsubscript{3}O\textsuperscript{+} is produced as the carbonic acid equilibrates -

\[ \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_2\text{O}^+. \]  
(2)

Titration using a pH meter will facilitate the observance of both equivalence points, since there are relatively few indicators that have two color transitions. A pH titration relies on the fact that the pH meter signal (specifically, the voltage developed at the glass electrode) depends primarily on the pH of the solution around the electrode, according to the Nernst equation

\[ E_{\text{glass}} = k - \frac{2.303RT}{F} p\text{H}, \]  
(12.5)

where T is the temperature, R is the ideal gas constant, F is the charge on a mole of electrons and k is an electrode specific constant.
Since the "pH" meter is actually measuring the voltage at the glass electrode (in mV), accurate output in pH units requires that the meter be calibrated. This adjusts the meter output for the impact of the unknown quantities, k and T. This is done by using solutions of known pH, i.e., standard acid-base buffers.

Once the meter is calibrated, the pH of the carbonate solution is easily followed as a function of the added HCl. Below pH 10.5 to 11, the electrodes are responding only to the \( H_3O^+ \) ions involved in the equilibria in equations 12.1 and 12.2. Addition of the \( H_3O^+ \) alters the amounts of \( CO_3^{2-} \) and \( HCO_3^- \) before the first equivalence point and the amounts of \( CO_3^{2-} \) and \( H_2CO_3 \) before the second equivalence point. These changes then alter the hydronium ion concentration, and pH.

Above pH 10.5 to 11, the glass electrode responds to other ions, such as \( Li^+ \), \( Na^+ \), and \( K^+ \), since so few \( H_3O^+ \) ions in solution. This effect is called the alkaline error since it appears that more hydronium ions are present (due to the response of the electrode to the other ions ) than really are.

Prelab Problems
1. If 0.1523 g of pure \( Li_2CO_3 \) (MW = 73.891 g/mol) are dissolved in aqueous solution, how many milliliters of 0.1012 M HCl is necessary to titrate to the first equivalence point? What is the volume required to reach the second equivalence point?

2. If 0.1480 g of a pure, unspecified carbonate compound requires 22.25 mL of 0.0976 M HCl to titrate to the second equivalence point, what are the molecular weight and most likely identity of the carbonate compound?

3. Sketch (show basic shape and equivalence point volumes) the titration curve you would expect for the titration of 25.00 mL of 0.0500M \( Na_2CO_3 \) using 0.100 M \( NaOH \). Name the type of solution being titrated and explain the equilibrium that governs the pH in each distinct region of the curve.

Procedure
1. The sample will have been dried for two hours at 110° C and stored in a dessicator. Weigh out three samples of about 0.15 g each to a precision of ± 0.1 mg, and transfer each sample to one of three 250-mL beakers. Dissolve in 75 mL of distilled \( H_2O \).

2. Calibrate the pH meter according to the instructions provided by the teaching assistant using the pH 4, pH 7, and pH 10 standard buffers. The electrode assembly should be rinsed with distilled water between measurements. Do not dry the electrode.

3. Fill the buret with your standardized HCl solution from Experiment 8.

4. Place a stirring plate under the electrode, leaving 2 to 3 inches of extra space. Then position the electrode in the beaker containing your sample, and place the beaker on the stirrer directly underneath the buret. Carefully start the stirring motor.
5. Make the initial buret reading, bringing the buret tip as close as possible to the solution’s surface.

6. Begin the titration. Add small increments of HCl, reading both the stabilized pH and the volume after every addition. Add enough acid to cause changes in pH of about 0.2 pH units. Try to make readings at roughly equal pH increments.

7. When the pH changes by more than 0.4 unit reduce the size of the HCl additions. As you near the equivalence point, the pH will change considerably upon the slightest addition of base. You may want to use the stirring rod to transfer titrant from the buret to the solution; this will enable you to add quarter drops until the endpoint is reached.

8. Once past the equivalence point, the pH changes will again be small. Continue titrating, adding enough acid to cause changes in pH of about 0.2 pH units, until you near the second equivalence point. When the pH again begins to change by more than 0.4 unit, reduce the size of the HCl additions until you are past the second equivalence point and again the pH changes are small.

9. Rinse the electrode, then repeat steps 4-8 with the next samples. (Do not lose the stir bar from the beaker when disposing of the titrated solution.)

10. Rinse the electrode and return it to the beaker containing pH 4 buffer. Do not let the electrode rest on the bottom of the beaker.

Report

1. Prepare a titration curve, graphing the volume of HCl added versus the pH at that volume. Read the values for the 1st and 2nd equivalence point from this curve.

2. Calculate the number of moles in each sample from your corrected titration volumes, using the average standardized molarity of HCl from Experiment 8.

3. Report the percent carbonate in each of your samples, the average percent carbonate and the standard deviation.

4. Based on the average percent carbonate in your sample, which alkali metal did your sample contain?

This experiment was adapted by Prof. S. Neal from Kennedy, J.H., Analytical Chemistry: Practice, 2nd ed., Saunders College Publishing, Orlando, FL: 1990. Last revision: 8/29/99