Experiment

ANALYSIS OF SODA ASH

The CCLI Initiative

Computers in Chemistry Laboratory Instruction

LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- understand the titration curve for a diprotic base.
- use the titration curve to calculate the percent of Na_2CO_3 in an unknown sample of soda ash.

BACKGROUND

Sodium carbonate is an important industrial chemical. It is used in the manufacture of soap, glass, paper and as a source of alkalinity, that is, as a base. About half the sodium carbonate used in the United States is manufactured by the Solvay process. In this process, which is carried out at 0 °C, carbon dioxide is bubbled through a concentrated sodium chloride solution which is saturated with ammonia. Sodium hydrogen carbonate precipitates from the solution and is isolated:

$$CO_{2(g)} + NH_{3(g)} + H_2O_{(l)} + Na^+_{(aq)} + Cl^-_{(aq)} \implies NaHCO_{3(s)} + NH_4^+_{(aq)} \ Cl^-_{(aq)} \quad (1)$$
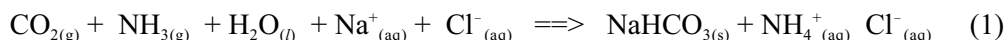
When heated to 300 °C, the sodium hydrogen carbonate decomposes to form sodium carbonate, carbon dioxide, and water.

$$2\ NaHCO_{3(s)} \implies Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)} \quad (2)$$
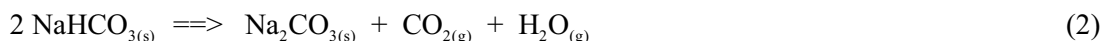
The crude product obtained from this thermal decomposition is called soda ash, which is primarily Na_2CO_3, although it also contains unreacted $NaHCO_3$ and other impurities.

The total acid neutralizing capacity of a soda ash sample, its alkalinity value, can be stated in terms of percent sodium carbonate. In doing so, any sodium hydrogen carbonate present in the sample is converted to its equivalent neutralizing capacity in terms of sodium carbonate. That is, a 100% $NaHCO_3$ sample is represented as a 50% Na_2CO_3 sample in terms of its acid neutralization capacity. It is sometimes convenient for chemical purposes to group compounds of similar behavior together and then state composition in terms of only one of them. For example, the potassium content of fertilizer is stated as percent K_2O, although the potassium compounds actually present may be phosphates, nitrates or carbonates. In this case the relating factor is the amount of potassium in a sample of fertilizer.

Carbonate ion and hydrogen carbonate ion are both sufficiently basic to be quantitatively determined by reaction with strong acid in a titration procedure. The neutralization of carbonate ion proceeds in two steps:

$$CO_3^{2-}{}_{(aq)} + H^+_{(aq)} \implies HCO_3^-{}_{(aq)} \text{ (hydrogen carbonate or bicarbonate)} \quad (3)$$
and

$$HCO_3^-{}_{(aq)} + H^+{}_{(aq)} \implies H_2CO_{3(aq)} \text{ (carbonic acid)} \tag{4}$$

Note that although we typically represent carbonic acid as H_2CO_3, in aqueous solution there is virtually no H_2CO_3 present. To be accurate we should represent H_2CO_3 as $CO_2 + H_2O$. Thus, the titration of $H_2CO_{3(aq)}$ with $H^+{}_{(aq)}$ is most accurately represented by the equation:

$$(H_2O + CO_2)_{(aq)} + 2\,OH^-{}_{(aq)} \implies CO_{2(g)} + 3\,H_2O_{(l)} \tag{5}$$
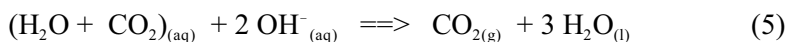
For convenience, we will adopt the normal convention of representing carbonic acid as H_2CO_3.

The titration curve shown here has two breaks as evidence of the two-step neutralization process. Note that the breaks are not as sharp as those obtained when a strong base is titrated with a strong acid. The first equivalence point, occurring at a pH of about eight, is not as well defined as the second, and consequently is not as useful for highly accurate analytical work. At the midpoint of the first break the principal species in solution is $HCO_3^-{}_{(aq)}$. The second equivalence point which corresponds to the formation of $H_2CO_{3(aq)}$ is more distinct and thus more useful for quantitative work.
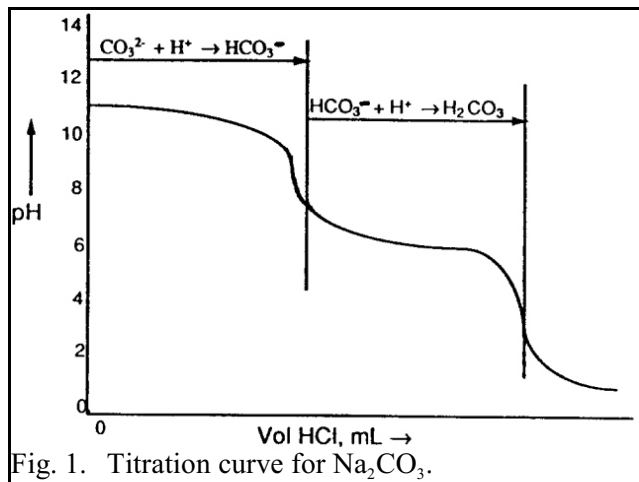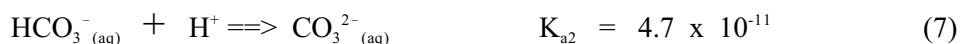

Fig. 1. Titration curve for Na_2CO_3.

The species in solution that determines the shape of the titration curve are the products of the stepwise titration, the hydrogen carbonate ion and carbonic acid. Both are weak acids with the following dissociation equilibria and dissociation constants:

$$H_2CO_{3\,(aq)} + H^+ \implies HCO_3^-{}_{(aq)} \qquad K_{a1} = 4.5 \times 10^{-7} \tag{6}$$

$$HCO_3^-{}_{(aq)} + H^+ \implies CO_3^{2-}{}_{(aq)} \qquad K_{a2} = 4.7 \times 10^{-11} \tag{7}$$

Notice that the two K_a values differ by four orders of magnitude. It is this relatively large difference that allows us to see both equivalence points on the titration curve. Because $HCO_3^-{}_{(aq)}$ is a much weaker acid than H_2CO_3 (or one could say, because $CO_3^{2-}{}_{(aq)}$ is a much stronger conjugate base than $HCO_3^-{}_{(aq)}$), nearly all the carbonate ion in the sample will be converted to $HCO_3^-{}_{(aq)}$ at the first equivalence point before the second step of the neutralization begins forming $H_2CO_{3(aq)}$.

SAFETY PRECAUTIONS

Safety goggles must be worn in the lab at all times. Any skin contacted by chemicals should be washed immediately.

BEFORE PERFORMING THIS EXPERIMENT . . .

1. Dry 1.5 grams of primary standard grade Na_2CO_3 for two hours at 110 °C.

2. Dry the unknown soda ash sample for two hours at 110 °C.

3. Boil one liter of deionized water and store in a capped Nalgene bottle.

As stated above, although soda ash is mostly Na_2CO_3, it contains some $NaHCO_3$. Given the fact that the two equivalence points show up on the titration curve, it should be possible to analyze for the percent Na_2CO_3 in the sample by using the first equivalence point. The reaction is:

$$CO_3{}^{2-}{}_{(aq)} + H^+{}_{(aq)} ==> HCO_3{}^-{}_{(aq)}.$$
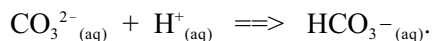
In going from the first to the second equivalence point the hydrogen carbonate reacts to form carbonic acid

$$HCO_3{}^-{}_{(aq)} + H^+{}_{(aq)} ==> H_2CO_3{}_{(aq)}.$$
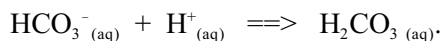
There are two sources of $HCO_3{}^-{}_{(aq)}$: the $HCO_3{}^-{}_{(aq)}$ formed from the $CO_3{}^{2-}{}_{(aq)}$ in the first step of the titration and the $HCO_3{}^-{}_{(aq)}$ from any $NaHCO_3$ present in the original sample. In principle we can calculate the amount of $HCO_3{}^-{}_{(aq)}$ formed from the $CO_3{}^{2-}{}_{(aq)}$ by knowing the moles of H^+ required to reach the first equivalence point. By subtracting this amount of $HCO_3{}^-{}_{(aq)}$ from the total $HCO_3{}^-{}_{(aq)}$ determined in the second step of the titration, we could then calculate the amount of $HCO_3{}^-{}_{(aq)}$ originally present in the sample.

Since the first equivalence point is not very distinct, it will be necessary to take the second derivative of the pH vs. volume curve to precisely define it. If you are not familiar with derivatives and how to obtain them, Your instructor should have a hand out which will assist you in understanding this.

EXPERIMENTAL PROCEDURE

Preparation of 0.1 *M* HCl

Standardized hydrochloric acid will be required in the analysis. Standardization will be accomplished by determining the volume of acid which reacts with a known quantity of a primary standard grade sodium carbonate in a titration procedure. By using a substance (Na_2CO_3) nearly identical to the unknown sample to standardize the acid, the effects of determinate errors will be minimized.

Prepare 1 L of approximately 0.1 *M* hydrochloric acid by adding 8.4 ml 12 *M* HCl to 1000 ml of deionized water. After mixing thoroughly, store in a stoppered glass bottle.

Calibration of drop size

In this experiment the volume of titrant will be determined by electronically counting the number of drops required to reach the equivalence point. Therefore, the volume of a single drop must be determined accurately. It is important that the rate of delivery of the hydrochloric acid used in the calibration part of the experiment is the same as that used during the actual titration. This insures that the drop size remains constant.

1. Your instructor will demonstrate how to set up the drop counter. Align the counter by filling the buret with the HCl solution and allowing it to drip through the counter into a small clean beaker. The buret is correctly aligned when the counter light on the interface flashes every time a drop falls from the buret. Alignment of the buret is a critical step in producing an accurate titration. Do not move the buret once it is aligned or serious error will result.

2. Load the program **Drop Counter Calibration** for drop calibration into the computer.

3. Use the instructions supplied by your instructor for calibration of your drop counter titration system, with a drop rate of two to four seconds per drop.

Calibration of the pH electrode

1.   Attach the pH electrode to the interface unit at the pH position and place the electrode in a buffer solution of pH 4. Click on **pH** in the **Variables View** and recalibrate your probe with the pH 4, 7 and 10 buffers supplied. Be sure to rinse the pH probe with distilled water after each buffer and before you place it in your analyte solution. Between titrations, the probe should be stored in the pH 7 buffer, then rinsed well with distilled water before inserting into your titration beaker.

Standardization of HCl

 Dissolve approximately 0.25 g of dry Na_2CO_3 in about 50 ml of boiled, deionized water in a 250 ml beaker. Be sure to record the exact mass of Na_2CO_3 used. Prepare two more samples in the same manner.

1.   Refill the buret with 0.1 M HCl. Check to be sure the alignment of the drop counter is still correct.

2.   Place a magnetic stirring bar in one of the sample solutions. Put the pH electrode into the solution taking care to position it out of the way of the stir bar. Place the container under the buret and counter assembly.

3.   The *MicroLAB* program for titration will be provided and is stored on the hard drive of your computer in the **Titrations** tab. Select the program indicted by your instructor. When everything is ready, click **Start** and turn on the Titration system.

4.   Remember to titrate at about the same drip rate as in the calibration, two to four seconds per drop.

5.   To maintain a constant head pressure keep the buret full by using a wash bottle to add 0.1 M HCl.

6.   Stop the experiment when the pH is approximately 11, and save it with a name you can identify later as your experiment.

Titration of an unknown soda ash sample

1.   Dissolve approximately 0.3 g (record the exact mass) of the unknown soda ash in about 80 ml of boiled, deionized water. Prepare two more samples in the same manner.

2.   Titrate each of your samples with your standardized HCl using the *MicroLAB* program indicated by your instructor and save it with a name you can identify each sample later.

3.   Rinse the pH electrode with deionized water when you are finished.

<center>DATA ANALYSIS</center>

Calibration of drop size

1.   Reload your calibration data into the *MicroLAB* program.

2.   Ensure that you are plotting ml vs. drops.

3.   Using this plot and the **Analysis** functions, construct a linear regression equation for your data to determine the equation necessary to convert drops to ml. Title your graph.

4.   After you have obtained the approval of your instructor, print the graph and record the calibration equation for use in your titrations.

Standardization of HCl

1.   Reload your standardization data into the *MicroLAB* program.

2.   Use the **Add Formula** to convert drops of HCl to ml HCl.

3.   Click-drag the formula to **Column C**, then to the **X** axis.

4.   Use the **Analysis** option to find the derivative of pH with respect to ml HCl at the first equivalence point. Add this to the **Y2** axis and scroll the **Spreadsheet View** to this approximate volume.

5.   Using the Analysis functions, obtain the second derivative of pH vs. Volume, drag this to the **Y-2** axis, and print out this graph for each titration.

6.   Use this information to determine the exact position of the second equivalence point. Print this graph and record its position on the graph. The volume to the second equivalence point should be exactly twice the volume to the first equivalence point.

7.   Determine the concentration of your HCl solution from the second derivative equivalence point and the mass of Na_2CO_3.

8.   Repeat this analysis for each standardization trial and average the values for the molarity of the HCl. Record this average for use in subsequent calculations.

Determination of the percent Na_2CO_3 in the unknown soda ash sample.

1.   Reload your data from the titrations of the unknown soda ash into the *MicroLAB* program.

2.   Use the **Analysis** options to construct first and second derivative plots for the first and second equivalence points for each titration of the soda ash unknown.

3.   Use your second derivative information to determine the first equivalence point for the titration of the unknown soda ash sample, then use the second derivative information to determine the second equivalence point for the titration of the unknown soda ash sample.

4.   Calculate the percent Na_2CO_3 and $NaHCO_3$ in each unknown soda ash sample and obtain the average value of each for the three analyses.