# Chemistry 213

ANALYSIS OF SODA ASH

LEARNING OBJECTIVES

The objectives of this experiment are to ...

- to understand the titration curve for a divalent base.

- to 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^oC, 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:

$$CO_2(g) + NH_3(g) + H_2O(l) + Na^+(aq) + Cl^-(aq) \rightarrow NaHCO_3(s) + NH_4^+(aq) + Cl^-(aq)$$
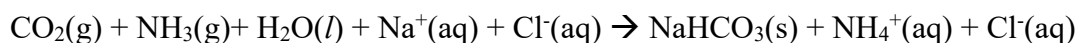
When heated to 300^oC, the sodium hydrogen carbonate decomposes to form sodium carbonate, carbon dioxide, and water.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

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 not uncommon to group compounds of similar behavior together and state the composition in terms of 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:

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \text{ (hydrogen carbonate or bicarbonate)}$$

and

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \text{ (carbonic acid)}$$

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 HCO_3^- with H^+ is most accurately represented by the equation:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$
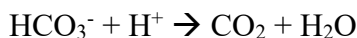
For convenience, we will adopt the normal convention of representing carbonic acid as H_2CO_3 .
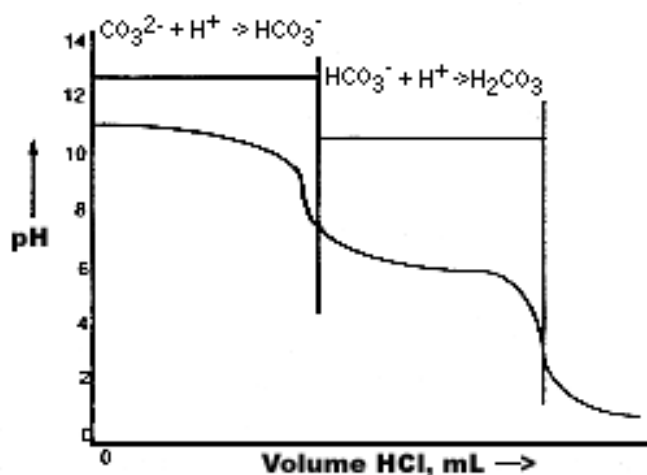
The titration curve shown above has two breaks as evidence of the two-step neutralization process. Note that the breaks are not as sharp as those obtained when a strong base is titrated with a strong acid. The first equivalence point, occurring at a pH of about 8, is not as well defined as the second, 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^-. The second equivalence point which corresponds to the formation of H_2CO_3 is more distinct and thus is more useful for quantitative work.

The species in solution that determine 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:

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \qquad K_{a2} = 4.7 \times 10^{-11}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad K_{a1} = 4.5 \times 10^{-7}$$

Notice that the two K_a values differ by about 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^- is a much weaker acid than H_2CO_3 (or one could say, because CO_3^{2-} is a much stronger conjugate base than HCO_3^-) nearly all the carbonate ion in the sample will be converted to HCO_3^- (at the first equivalence point) before the second step of the neutralization begins forming H_2CO_3

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.   Standardized HCl has been provided.

2.   The unknown soda ash sample has also been dried for two hours at $110^{\circ}C$.

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

However, we cannot carry out these calculations very accurately because the first equivalence point is not very distinct. That is, because the pH change at the first equivalence point is not very dramatic, we have trouble accurately specifying the exact volume of acid required to reach the first equivalence point. To avoid this problem we will use the more distinct second equivalence point and report the acid neutralizing ability of the soda ash sample in terms of percent Na_2CO_3 (even though a small part of the neutralizing ability of the sample really comes from $NaHCO_3$). In other words we will assume that the number of moles of Na_2CO_3 in the soda ash sample equals one-half the number of moles of strong acid required to reach the second equivalence point.

EXPERIMENTAL PROCEDURE

Calibration of the pH electrode

Attach the electrode to pH meter and calibrate with buffer solutions of pH 7 and pH 4.

Titration of an Unknown Soda Ash Sample

1. Dissolve approximately 0.20 g (record the exact mass) of the unknown soda ash in about 80 mL of deionized water.   Add five drops Indicator. Prepare four more samples in the same manner.

2. The first titration is used to determine the pH at the second equivalence point. Add HCl from the buret at regular intervals, while recording the pH, until the titration has leveled off after the second equivalence point. Make sure to reduce volume additions in the equivalence point regions. Graph pH verses volume HCl added in excel and determine the pH and indicator color at the second equivalence point. It is critical that the pH at the second equivalence point is determined accurately. *Include this graph in your data sheet.*

3. Rinse the pH electrode with deionized water and titrate the rest of the samples to the end ppoint using the indicator color and pH determined in previous step.

4. Your score will be based on the precision and accuracy of the measurements you make. If it appears you do not have a high degree of precision you may want to consider performing more trials (assuming some soda ash sample remains).

DATA ANALYSIS

Determination of the percent Na$_2$CO$_3$ in the Unknown Soda Ash Sample

1. Calculate the percent Na$_2$CO$_3$ in the unknown based on the average value of the five analyses. Make sure to record sample identification number.
2. Include data sheet and titration graph in your report.

<table>
<tr><td>Points will be added or subtracted from total based on accuracy of results.

Make sure to list Sample Identification Number in the results section of your report.</td><td colspan="2"></td></tr>
</table>

Experimental Value is within ___ % of Actual Value	**Points**
< 0.1	**+2**
< 1.0	**0**
< 2.0	**-2**
< 5.0	**-3**
< 10 .0	**-5**
< 20.0	**-7**
> 20.0	**-10**

Name(s) _____,_____,_____.

Section_____

ANALYSIS OF SODA ASH

Molarity of the standardized HCl _____M

Analysis of Unknown Soda Ash

Unknown Identification # _____

		Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Initial mass of soda ash	(g)					
Volume of titrant (HCL) added. (2nd Eq. Point)	(mL)					
Moles of Na_2CO_3 in sample						
Mass of Na_2CO_3 in sample	(g)					
% Na_2CO_3 in sample						

Average Percent Na_2CO_3 _____

Titration was carried out to a pH of _____ at the 2nd equivalence point.

Show calculation to determine percent sodium carbonate in trial one:

Discuss the precision of the results obtained.

What can be said in regards to the accuracy of the results? Explain.