Determination of the Percentage of Sodium Carbonate in an Unknown Carbonate Mixture

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Abstract

A hydrochloric acid (HCl) titrant solution was made and standardized using known quantities of dried sodium carbonate (Na₂CO₃). The concentration of the HCl solution was calculated to be 0.1002±0.0006 M. A solution of a mixture of potassium carbonate and sodium carbonate was made and three titrations of it were carried out, data from two of which were used to calculate the fractions of Na₂CO₃ and K₂CO₃ in the unknown. The fraction of Na₂CO₃ in the unknown was calculated to be 0.7568±0.0064, with the mass of Na₂CO₃ in the sample determined to be 0.7576±0.0064 g. The mass of K₂CO₃ in the sample was 0.2435±0.0064 g. The pH vs. HCl added of the titration of Na₂CO₃ with HCl was graphed and compared to a theoretical curve. The curves were similar in shape and in the endpoint regions, but differed in the buffer regions. The difference was attributed to the dissolved CO₂ in the experimental solution that was unaccounted for in the calculated theoretical curve.

Introduction

Polyprotic acids and their conjugated bases are commonly used in industry and in research. They are also common in household applications. For example, solutions containing carbonate ions, CO₃²⁻, and bicarbonate ions HCO₃⁻, are routinely used for cleaning, cooking, laundry, preparation of carbonated beverages, disinfection, neutralization of acids, etc. Therefore, analytical determination of carbonates has many important applications.

The CO₃²⁻ and HCO₃⁻ can be viewed as conjugated bases of HCO₃⁻ and H₂CO₃ (carbonic acid), respectively. Therefore, the concentration of CO₃²⁻ in water can be determined using titration with a strong acid, such as HCl. This titration process is not trivial as the final product of the titration, carbonic acid, can also be produced by dissolving atmospheric CO₂ in water. Therefore one must take care to remove CO₂ from all solutions during the titration.

\[
\begin{align*}
\text{CO}_3^{2-} + \text{H}_3\text{O}^+ & \rightarrow \text{HCO}_3^- + \text{H}_2\text{O} \quad \text{(the first equivalence point)} \\
\text{HCO}_3^- + \text{H}_3\text{O}^+ & \rightarrow \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \quad \text{(the second equivalence point)} \\
\text{H}_2\text{CO}_3 & \leftrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O} \quad \text{(the equilibrium complicating this titration)}
\end{align*}
\]

The primary educational goal of this project is to learn how to generate a theoretical titration curve for a conjugate base of a polyprotic acid using different types of approximations. This kind of calculations nicely illustrates the concepts of equilibria in the solutions containing acids and their conjugate bases. The actual sample used in the analysis is a mixture of two carbonates, Na₂CO₃ and K₂CO₃, mixed in an unknown proportion. The secondary goal of this project is to determine this proportion and conduct an appropriate error analysis.

Experimental Section

The first part of the experiment was to make all the solutions to be titrated. 500 mL nanopure water was boiled and cooled to room temperature. The container of water was kept sealed at all times after boiling. A dilute hydrochloric acid solution was made by adding 4.2 mL concentrated HCl to a 500 mL volumetric flask, then adding nanopure water to the line. Standardization solutions were made by weighing out three 0.15 g samples of dried sodium carbonate and placing each in a 250 mL Erlenmeyer flask. 50 mL of boiled and cooled nanopure
water was added to each flask, the Na₂CO₃ was dissolved, and the flasks were stoppered until there were ready to be titrated.

To make the unknown solution, first the vial holding the unknown was taken out of the oven, capped, and allowed to cool. The vial with the cap and unknown were weighed, the unknown solid was transferred carefully to a 100 mL volumetric flask, and boiled and cooled nanopure water was added to the flask up to the line. The empty vial and cap were then weighed again to determine the mass of unknown transferred to the flask. The solution was stoppered until used.

The Na₂CO₃ solution for titration with the pH meter was made by dissolving 0.00200 moles of Na₂CO₃ in 50.0mL of boiled and cooled nanopure water in a 250mL Erlenmeyer flask. The solution was stoppered until used.

The pH meter was calibrated using buffer solutions in the order of pH 10, 7, then 4 to make it most accurate in the acidic range. To determine the indicator correction, 0.302 g sodium chloride was dissolved in 100 mL boiled and cooled nanopure water in a beaker. Six drops of phenolphthalein and ten drops of bromocresol green were added, along with a stir bar. The solution was titrated with the dilute HCl solution until it changed from light blue to light green. The amount of HCl titrated is the indicator correction.

Three standardizations of the HCl solution were carried out. The first standardization was performed quickly to find the end points, while the next two were performed slowly and the data used to determine the HCl concentration of the titrant. In each case, the analyte solution began as a magenta solution until it neared the first endpoint, when it turned dark blue. The volume of titrant added was noted. Between the first and second end points, the analyte solution was a light turquoise. Near the second endpoint, the solution turned slightly green. At this color change, it was boiled for approximately two minutes, then stoppered and cooled to room temperature. The solution returned to a turquoise blue following boiling. The titration was then continued until the solution turned a slightly yellowish green. From the endpoint values of the two slow standardization titrations, the concentration of the HCl titrant was calculated.

Once the titrant was standardized, titration of the unknown solution was carried out. Again, there were three titrations, the first fast to determine the endpoints and last two slow to collect data for analysis. In each case, 25.0 mL of the unknown solution was measured using a volumetric pipette and transferred to a 250 mL Erlenmeyer flask. Again, six drops of phenolphthalein and ten drops of bromocresol green were added, along with a stir bar. Titration of the unknowns was carried out following the same procedure as for the standardizations.

Finally, titration of a known amount of sodium carbonate was carried out using a pH meter (sensitivity of 0.01 pH units) to monitor the change in pH with volume of titrant added. Again, six drops of phenolphthalein and ten drops of bromocresol green were added to the flask, along with a stir bar. The titrant was added in small aliquots and the pH was monitored between additions. Near the endpoints, as determined by increasingly large changes in pH, the amount of titrant added was slowed to dropwise. Near the second endpoint, the analyte solution was boiled, then capped and cooled. The titration was continued until well past the second endpoint in order to gather data for a titration curve spanning a wide range of pH values (1).

Burette calibration results from lab 1 were not applied because they were suspect in my case. All volumes below refer to uncorrected volumes read directly from the burette.
Results

_Titration with the indicator._ The titration of the blank showed a _0.05mL correction_ was necessary. This volume of HCl was _subtracted from all other titration volumes_ to account for the HCl used to titrate all the components of the analyte solutions except the species actually being studied (components such as the water and indicators). All the data reported below have been corrected. Three standardization titrations were performed, but only data from the second two were used to determine the concentration of the HCl titrant. This is because the first one was performed quickly, and was not as accurate. The endpoint was more yellow for the first titration, suggesting it had gone past the real endpoint, and a quick calculation of the molarity from the first titration data showed it to be significantly different from the two subsequent titrations (a maximum difference of 0.008 M). The two slow standardizations of the HCl solution differed by only 0.25 mL (Table 1). The calculated concentration of the titrant was _0.1002±0.0006 M_ (Table 2). Excel functions were used for all calculations. The Excel “average” function was used to find the mean and the “stdev” function was used to determine the error.

Table 1: Standardization data and calculated concentration of HCl titrant for each standardization titration. Molecular weight used for Na₂CO₃ is 105.987 g/mol

<table>
<thead>
<tr>
<th>STANDARDIZATION</th>
<th>Trial 1 (not used)</th>
<th>Trial 2</th>
<th>Trial 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃ weight (g)</td>
<td>0.1520</td>
<td>0.1510</td>
<td>0.1510</td>
</tr>
<tr>
<td>HCl volume (mL)</td>
<td>27.50</td>
<td>28.60</td>
<td>28.35</td>
</tr>
<tr>
<td>Corrected HCl vol. (mL)</td>
<td>27.45</td>
<td>28.55</td>
<td>28.30</td>
</tr>
<tr>
<td>HCl concentration (M)</td>
<td>0.1045</td>
<td>0.0998</td>
<td>0.1007</td>
</tr>
</tbody>
</table>

Table 2: Calculated average, standard deviation, and %RSD for the HCl concentration.

<table>
<thead>
<tr>
<th>Mean (M)</th>
<th>st. dev. (M)</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1002</td>
<td>6.2E-04</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Titration of the unknown mixture was then carried out. Data from the second two titrations (the slow ones) were used to determine the total carbonate ion concentration in the unknown mixture. The two slow titrations were within 0.05 mL of each other, suggesting reproducibility of titration endpoint (Table 3). The total moles of carbonate ion in the unknown mixture was calculated to be 0.00891(1) moles (the number in parenthesis represent uncertainty in the last digit). All calculations were performed with Excel functions. The average function was used to find the mean and the stdev function was used to determine the error.

Table 3: Calculation of total moles CO₃²⁻ in unknown mixture.

<table>
<thead>
<tr>
<th>UNKNOWN</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total weight of unknown (g)</td>
<td>1.0011</td>
</tr>
<tr>
<td>Second Titr. (slow)</td>
<td></td>
</tr>
<tr>
<td>Vol. of Unknown Sol. (mL)</td>
<td>25.00</td>
</tr>
<tr>
<td>Weight of Unknown in Sol. (g)</td>
<td>0.2503</td>
</tr>
</tbody>
</table>
Table 4: Calculated mean, standard deviation, and %RSD for moles of total carbonate anion in the unknown mixture.

| Total moles of $\text{CO}_3^{2-}$ in the unknown solution |
|-----------------|-----------------|--------------|
| Mean (mol)      | St. Dev. (mol)  | %RSD        |
| 8.91E-03        | 1.41E-05        | 0.159       |

**Titration with the pH meter.** The result of the titration of 0.00200 moles of Na$_2$CO$_3$ with HCl using a pH meter is shown in Figure 1. This titration curve is typical of the titration of a polyfunctional base. There are two clearly discernable inflection points, at around 20 mL and 40 mL, which correspond to the $\text{CO}_3^{2-} \rightarrow \text{HCO}_3^-$ and $\text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3$ equivalence points, respectively. There are what at first sight appears to be two outlying data points that occur at about 40.00 mL HCl added and pH 6. These two points are in fact the spike of pH that occurs after the analyte was boiled to get rid of any residual carbon dioxide.

**Figure 1:** Titration of 0.002 moles Na$_2$CO$_3$ with 0.100M HCl.
Discussion

**Composition of the unknown mixture.** The calculated total moles of CO$_3^{2-}$ in the unknown mixture and the total measured mass of the unknown are sufficient to determine the fraction of Na$_2$CO$_3$ ($\alpha$) in the original mixture. The equations used for this calculation was taken from the discussion notes (2):

\[
n_{\text{carbonate}} = \frac{1}{2} \times C_{\text{HCl}} \times V_{\text{HCl added}} \times \left( \frac{V_{\text{unknown}}}{V_{\text{unknown used for titration}}} \right) \quad (1)\]

\[
\alpha = \left[ \frac{n_{\text{carbonate}}}{m_{\text{total}}} - \frac{1}{MW_{\text{K2CO3}}} \right] / \left[ \frac{1}{MW_{\text{Na2CO3}}} - \frac{1}{MW_{\text{K2CO3}}} \right] \quad (2)
\]

Here, $\alpha$ is the fraction of Na$_2$CO$_3$ in the total mass of the unknown; $1 - \alpha$ is the corresponding fraction of K$_2$CO$_3$ in the unknown; MW stands for molecular weight; and $m_{\text{total}}$ is the full mass of the unknown sample. The error was calculated by the propagation of errors using the textbook approach (3). The standard deviation in the number of moles of CO$_3^{2-}$ was estimated from the standard deviations in the volume and the concentration of the HCl titrating solution (the small errors in $V_{\text{unknown}}$ and in $V_{\text{unknown used for titration}}$ are neglected):

\[
\sigma_{\text{carbonate}} = n_{\text{carbonate}} \times \left[ \frac{(\sigma V/V_{\text{HCl added}})^2 + (\sigma C/C_{\text{HCl}})^2}{2} \right]^{0.5} \quad (3)
\]

After that, the standard deviations in $\alpha$ and in the actual masses of Na$_2$CO$_3$ and K$_2$CO$_3$ in the unknown were calculated. Note that these equations neglect the error in weighing the unknown sample because it is expected to be much less significant than the error in the titration volumes.

\[
\sigma_{\alpha} = \left( \frac{\sigma_{\text{carbonate}}}{m_{\text{total}}} \right) / \left[ \frac{1}{MW_{\text{Na2CO3}}} - \frac{1}{MW_{\text{K2CO3}}} \right] \quad (4)
\]

\[
\sigma_{m\text{Na2CO3}} = \sigma_{m\text{K2CO3}} = \sigma_{\alpha} \times m_{\text{total}} \quad (5)
\]

Table 5 shows the results of these calculations, which were done in Excel. The fraction of Na$_2$CO$_3$ in the mixture was determined to be 0.7568±0.0064, and the fraction of K$_2$CO$_3$ was calculated to be 0.2432±0.0064. These fractions correspond with the sample containing 0.7576±0.0064 g of Na$_2$CO$_3$ and 0.2435±0.0064 g of K$_2$CO$_3$.

**Table 5:** Fraction and mass of K$_2$CO$_3$ and Na$_2$CO$_3$ present in the unknown mixture.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Mass of Unknown (g)</td>
<td>1.0011</td>
<td>neglected</td>
</tr>
<tr>
<td>MW of K2CO3 (g/mol)</td>
<td>138.207</td>
<td>none</td>
</tr>
<tr>
<td>MW of Na2CO3 (g/mol)</td>
<td>105.987</td>
<td>none</td>
</tr>
<tr>
<td>Fraction of Na2CO3 in Unknown</td>
<td>0.7568</td>
<td>0.0064</td>
</tr>
<tr>
<td>Fraction of K2CO3 in Unknown</td>
<td>0.2432</td>
<td>0.0064</td>
</tr>
<tr>
<td>Mass of Na2CO3 in Unknown (g)</td>
<td>0.7576</td>
<td>0.0064</td>
</tr>
<tr>
<td>Mass of K2CO3 in Unknown (g)</td>
<td>0.2435</td>
<td>0.0064</td>
</tr>
</tbody>
</table>
**Theoretical titration curve.** The theoretical titration curve was generated using the experimental HCl molarity, weight of Na\textsubscript{2}CO\textsubscript{3}, and volume of HCl added (Figure 2). Five different equations were used to create the theoretical titration plot. All calculations were carried out in Microsoft Excel. The equations for the regions before the first equivalence point, between the first and second equivalence points, and after the second equivalence point were taken from the discussion notes (2). For calculation of the pH at the first and second endpoints, equations from the textbook were used (3). All equations are reproduced below.

It is convenient to first define the total volume of the solution during the titration, and the effective initial concentrations of the carbonate and HCl before they start neutralizing each other. In the equations below, \( V^o_{\text{carbonate}} \) is the initial volume of the titrated solution, and \( V_{\text{HCl}} \) is the volume of the added titrant.

\[
V_{\text{total}} = V^o_{\text{carbonate}} + V_{\text{HCl}} \quad (6)
\]

\[
C_{\text{carbonate}} = [\text{Na}_2\text{CO}_3]^o \times \left(\frac{V^o_{\text{carbonate}}}{V_{\text{total}}}\right) \quad (7)
\]

\[
C_{\text{HCl}} = [\text{HCl titrant}] \times \left(\frac{V_{\text{HCl}}}{V_{\text{total}}}\right) \quad (8)
\]

The initial pH can be calculated by treating the system as a solution of Na\textsubscript{2}CO\textsubscript{3} (weak base):

\[
[\text{OH}^-]/[\text{Na}_2\text{CO}_3]^o = K_{b1} = K_w/K_{a2} \quad (9a)
\]

\[
p\text{OH}^- = -\log[\text{OH}^-] = 14 - p\text{OH} = pH \quad (9b)
\]

Before first equivalence point, the system can be approximately treated as a HCO\textsubscript{3}^-/CO\textsubscript{3}\textsuperscript{2-} buffer:

\[
[\text{CO}_3^{2-}] \sim C_{\text{carbonate}} - C_{\text{HCl}} \quad (10a)
\]

\[
[\text{HCO}_3^-] \sim C_{\text{HCl}} \quad (10b)
\]

\[
[H_3O^+] = K_{a2} \times [\text{HCO}_3^-]/[\text{CO}_3^{2-}] \quad (10c)
\]

At the first equivalence point, the system can be approximately treated as a solution of NaHCO\textsubscript{3} with [NaHCO\textsubscript{3}] = \( C_{\text{carbonate}} \) (see chapter 15D of the textbook):

\[
[H_3O^+] \sim \{(K_{a2} \times C_{\text{carbonate}} +K_w)/(1 + C_{\text{carbonate}}/K_{a1})\}^{0.5} - (K_{a1} K_{a2})^{0.5} \quad (11)
\]

The last equality is an approximation but it is appropriate in this case as \( K_{a1} = 4.2 \times 10^{-7} \); \( K_{a2} = 4.7 \times 10^{-11} \), and therefore \( K_{a2} \times C_{\text{carbonate}} \gg K_w \) and \( C_{\text{carbonate}}/K_{a1} \gg 1 \).

Between first and second equivalence points, the system can be approximately treated as a H\textsubscript{2}CO\textsubscript{3}/HCO\textsubscript{3}^- buffer:

\[
[\text{HCO}_3^-] \sim 2 \times C_{\text{carbonate}} - C_{\text{HCl}} \quad (12a)
\]

\[
[H_2\text{CO}_3] \sim C_{\text{HCl}} - C_{\text{carbonate}} \quad (12b)
\]

\[
[H_3O^+] = K_{a1} \times [H_2\text{CO}_3]/[\text{HCO}_3^-] \quad (12c)
\]

At the second equivalence point, the system can be treated as solution of carbonic acid with \( [H_2\text{CO}_3] = C^o_{\text{carbonate}} \). The pH can be calculated from the weak acid approximation:

\[
[H_3O^+] \sim \{K_{a1} \times C_{\text{carbonate}}\}^{0.5} \quad (13)
\]

After second equivalence point, the pH can be calculated from the excess HCl added:

\[
[H_3O^+] \sim C_{\text{HCl}} - 2 \times C_{\text{carbonate}} \quad (14)
\]
Figure 3: Comparison of the experimental and theoretical titration curves. The disagreement is likely due to the dissolved CO₂ (there is no disagreement after boiling the solution)

The comparison of the two curves shows that the experimental data were somewhat inconsistent with the calculated curve until after the second equivalence point. After the second equivalence point, they match up almost perfectly. This inconsistency is probably due to the buffer effect of dissolved carbon dioxide in the water used to make the HCl solution (which is neglected in this calculation). All the water for the analyte solutions was boiled to get rid of dissolved CO₂, but the water for the HCl dilution was not. This means that during the titration, some CO₂ was being added to the analyte. This CO₂ acted as a buffer, causing there to be a smaller change in pH when titrant was added, somewhat flattening out the experimental titration curve. The experimental curve is slightly more acidic than it should be until after the first endpoint, at which it become slightly more basic than it should be. The carbonate anion being analyzed also acts as a buffer, of course, but its presence and concentration are already known. The additional unknown CO₂ is what makes the experimental titration curve differ from the theoretical one. The presence of CO₂ in the analyte is shown by the spike when it was boiled. The increase in pH after boiling is a result of CO₂ being expelled. There is no such spike in the theoretical curve because the calculations for the theoretical curve are assuming perfect conditions, including no unknown amount of CO₂ dissolved in the solution.

Another source of error, especially in the basic pH region, is the pH meter. Even though it was calibrated, it is very slow and sometimes finicky. It nearly always changed pH by +/-0.01 units when my hand got near it, and would change back when my hand moved away. Since the pH meter was calibrated with the most accuracy in the acidic range (the progression of calibrating buffers was pH 10, 7, 4), it would be more inaccurate in the basic region than in the acidic region.

**Special points during the titration.** Data from the theoretical curve and the experimental curve were used to determine the experimental and theoretical pH before any HCl was added, midway to the first equivalence point, at the first equivalence point, midway between the first and second equivalence points, at the second equivalence point, and after excess HCl was added.
The pH of the initial solution, halfway to the first equivalence point, midway between the first and second equivalence points, and with excess HCl were calculated using equations from the textbook (3). The pH at the first and second titration points was already calculated for use in the theoretical titration curve. The measured equivalence points were determined by the color change of the analyte. At the first equivalence point, the analyte went from purplish pink to dark blue. At the second equivalence point the analyte went from turquoise to greenish yellow.

Table 6: pH calculated at varying points during the experimental and theoretical titrations.

<table>
<thead>
<tr>
<th>pH at</th>
<th>Measured</th>
<th>Expected</th>
<th>Use equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Solution</td>
<td>11.19</td>
<td>11.46</td>
<td>9</td>
</tr>
<tr>
<td>Halfway to 1st Equivalence Point</td>
<td>9.96</td>
<td>10.62</td>
<td>10</td>
</tr>
<tr>
<td>1st Equivalence Point</td>
<td>8.23</td>
<td>8.35</td>
<td>11</td>
</tr>
<tr>
<td>Middle Between 1st and 2nd Equiv. Points</td>
<td>6.71</td>
<td>6.68</td>
<td>12</td>
</tr>
<tr>
<td>2nd Equivalence Point</td>
<td>4.93</td>
<td>4.02</td>
<td>13</td>
</tr>
<tr>
<td>Excess HCl</td>
<td>2.47</td>
<td>2.49</td>
<td>14</td>
</tr>
</tbody>
</table>

The measured and expected pH at different points are generally different, except near the very end when there is excess HCl and midway between the two equivalence points. As discussed above, the difference is most likely do to the CO₂ dissolved in the analyte that was unaccounted for. This is why the numbers match the most at excess HCl – all the CO₂ is boiled off and the pH meter is quick to respond to changes in pH.

During the experimental titration, the color changes observed matched the inflection points of the curve well. Before any titrant was added, the analyte was a bright magenta. During the first buffer region, prior to the first endpoint, the solution became increasingly blueish, losing its pink color. Around pH 8.35, the solution began to turn blue, finally becoming a dark blue at pH 8.23. The pH meter also took a long time to settle on a reading. The color change indicates the first equivalence point was reached at pH 8.23. Following this, the solution quickly became a bright turquoise color. This color stayed the same until nearing pH 5.34, when it began to become greenish. At pH 5.34, it was a very light bluish green. At this point I boiled the solution and it turned back to turquoise. After adding only 7 drops of titrant, it turned greenish yellow, at pH 4.93. This indicates it was the second equivalence point. The point at which enough moles of HCl were added to completely neutralize the measured moles of carbonate in the solution was at pH 5.83, according to simple calculations of how many moles of HCl were added. The true second equivalence point is probably closer to pH 4.93 than it is to pH 5.83, as indicated by the theoretical curve, which puts it at pH 4.02. The pH meter probably had not completely equilibrated before I took the reading. I waited about five minutes, but sometimes the pH meter is amazingly slow at equivalence points so it is possible I still took a reading too fast. After this point, the solution became a light yellow color, indicating there was excess HCl.

**Summary**

It was calculated that the unknown sample contained 0.7576±0.0064 g of Na₂CO₃ and 0.2435±0.0064 g of K₂CO₃. The titration of 0.002 moles Na₂CO₃ produced an experimental titration curve that had the same shape and similar endpoints as the theoretical curve, but differed
in the buffer regions. This is most probably due to CO$_2$ added through the titrant. For this portion of the lab, it would be best to boil all the water, because then it can be assumed that there is no unaccounted for CO$_2$ in any solution. Another improvement for this lab would be to use a faster responding pH meter.

References

(2) Chemistry 151L Week 3 Discussion Slides, Fall 2008. Nizkorodov, S. https://eee.uci.edu/08f/40750/