

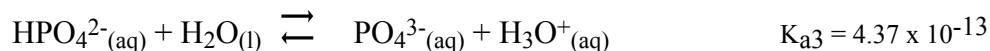
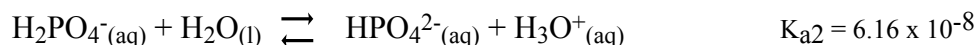
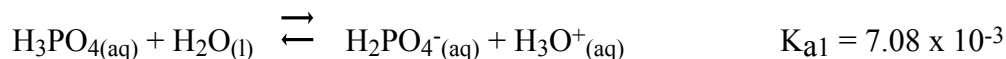
Polyprotic Systems

Introduction

Until now you have dealt primarily with monoprotic acids such as hydrochloric and nitric acid in the laboratory. This leaves an entire world of polyprotic acids unexplored. Polyprotic acids, acids that have more than one acidic proton, are common. For example, you have worked with sulfuric acid and with KHP that comes from diprotic phthalic acid. In this experiment, you will trace out the entire titration curve of the diprotic acid carbonic acid H_2CO_3 . Carbonic acid is made by dissolving carbon dioxide CO_2 in water. In addition to the environmental presence of carbonic acid formed by dissolving the CO_2 from the air into water or by acidifying waters that have percolated through formations containing carbonate minerals, the carbonic acid system plays another major role in the respiration of all animals, including humans. The equilibrium among $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{HCO}_3^-(\text{aq})$, and $\text{CO}_3^{2-}(\text{aq})$ is critical for the proper transport of CO_2 , formed in the metabolic cycle inside cells, through the blood stream to be expelled by the lungs. While carbonic acid is not a strong acid by the dissociation definition, it is corrosive and does react with metals to form carbonates. In this experiment, we will start with Na_2CO_3 and add acid, detecting the formation of each of the two endpoints of the titration curve using a pH meter.

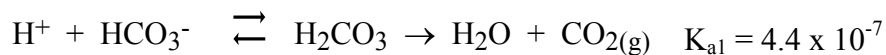
One aspect of polyprotic acids that is different from monoprotic acids is that they always make buffer solutions. Think about your list of strong acids; all but sulfuric acid are monoprotic, and only the first proton of sulfuric acid is considered strong. This buffering action can make experiments more complicated. In the experiment you are about to perform, titration of the first endpoint that you encounter establishes a buffer solution that complicates the analysis and determination of K_a for that equivalence point. We should note here that this buffering action can also be used to your benefit. Some reactions take place only in a specific pH range, and buffers can be used to maintain this pH during an experiment. You will be examining the nature of buffer solutions in the next experiment in the series on acid-base chemistry.

Polyprotic acids can generate very complex systems at equilibrium. For example, phosphoric acid undergoes three separate dissociations:



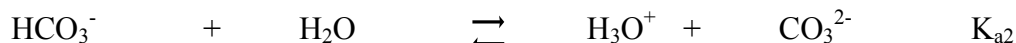
Each of these dissociations is an equilibrium reaction with an acid dissociation constant. As a result, calculating the concentrations of the species present in a phosphoric acid solution can become quite involved. Nevertheless, salts of phosphoric acid are commonly used for the preparation of buffer solutions in biochemical studies.

The important acid-base reactions for carbonate are:



We have written the acid dissociation reactions in the reverse sense from usual to emphasize that we are working in this sense, starting from a solution of Na_2CO_3 . Also notice that during the titration you will encounter the equivalence point of the **second** proton (K_{a2}) of diprotic carbonic acid as the first equivalence point in the titration. It occurs at high pH. The **first** proton (K_{a1}) is encountered as the second equivalence point in the titration. It occurs at low pH. One of the goals of this experiment will be to make your own determinations of the two acid dissociation constants of carbonic acid.

Because of the polyprotic nature of carbonic acid, the equilibrium analysis necessary to develop the formulas for reduction of measurements of the pH into the acid dissociation constant are somewhat involved for the second proton equilibrium (the first equivalence point that you will encounter in the titration). We will not go through the details of the development, but will just describe for you how to find the final formulas. You may want to go through the development on your own, using the discussion as an aid to prove to yourself that the formulas are correct. At the second proton equivalence point, the solution is identical in composition with a solution of the sodium salt of the bicarbonate ion HCO_3^- (except for some extra dissolved $\text{NaCl}(\text{aq})$). An Equilibrium treatment of the pH of that solution will yield precisely the formulas we need to work with. The dominant species equilibria to be considered are:



We start by writing down the two conditions that are commonly referred to as a mass balance and a charge balance. The mass balance sets the sum of all carbonate containing species equal to the total concentration in the original sample as diluted to the present volume. The charge balance sets the sum of the concentrations of all positively charged species equal to the sum of the concentrations of all the negatively charged species (including the sodium cation needed for NaHCO_3). These two conditions are combined into an equality that must be observed. We then use the two equilibrium expressions above and the K_w equilibrium to re-express $[\text{H}_2\text{CO}_3]$, $[\text{CO}_3^{2-}]$, and $[\text{OH}^-]$ and insert these into the combined equality. The combined equality is then simplified and rearranged to get the result:

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_{a2}[\text{HCO}_3^-] + K_w}{1 + \frac{[\text{HCO}_3^-]}{K_{a1}}}}$$

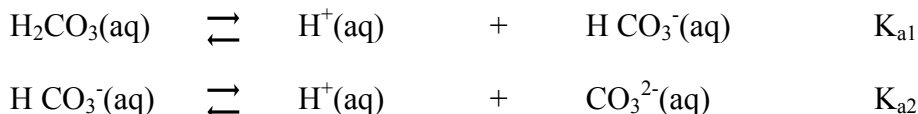
While this formula looks difficult to work with, the specific circumstances of the carbonic acid equivalence point simplify it greatly. Firstly for convenient laboratory concentrations, and specifically for those used in this experiment, it will be true that $[\text{HCO}_3^-] \gg K_{a1}$. Consequently, we may neglect the unity in the denominator.

Further, it will also be the case that $K_{a2}[\text{HCO}_3^-] \gg K_w$, so that K_w may be neglected in the numerator. Canceling and simplifying then gives:

$$[\text{H}_3\text{O}^+] = \sqrt{K_{a1}K_{a2}}. \quad (1)$$

While this does not give us either of the acid constants directly, if we know one of them, we can use this relationship to determine the other.

From the equilibrium at the second equivalence point we get the necessary additional information that enables the determination of both acid dissociation constants. At the second equivalence point the solution has had two equivalents of protons added to the analyte. For purposes of consideration of the pH equilibria, the solution is then simply that of carbonic acid H_2CO_3 (with some extra NaCl in solution that does not affect the acid equilibria).



A fairly quick solution of these equilibria is available if $K_{a1} \gg K_{a2}$ because then we may assume that the $[\text{H}^+]$ concentration arises dominantly from the first equilibrium and then $[\text{H}^+] = [\text{HCO}_3^-]$. Writing the equilibrium constant expressions:

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad ; \quad K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

Rearranging these expressions:

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_{a1}} \quad ; \quad [\text{HCO}_3^-] = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{K_{a2}}$$

Using substitution:

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+]^2[\text{CO}_3^{2-}]}{K_{a1}K_{a2}}$$

Since $[\text{H}^+] = [\text{HCO}_3^-]$, and solving for $[\text{CO}_3^{2-}] = \frac{[\text{HCO}_3^-]}{[\text{H}^+]} K_{a2} = K_{a2}$.

This leads to reduces the expression for $[\text{H}_2\text{CO}_3]$ to:

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+]^2}{K_{a1}}$$

Now in a solution that is M molar in H_2CO_3 , we must have :

$$[\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3] = M$$

$$[\text{H}_2\text{CO}_3] = M - \{ [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \}$$

Since we are dealing with weak acid dissociation constants, we can expect

$$[\text{HCO}_3^-] + [\text{CO}_3^{2-}] \ll M, \text{ hence}$$

$[\text{H}_2\text{CO}_3] = M$. Using the concentrations in the expression for K_{a1}

$$K_{a1} = \frac{[\text{H}^+]^2}{M} \quad (2)$$
$$[\text{H}^+] = \sqrt{MK_{a1}}$$

In the titration, $M = a/(V + v)$, where $a = g/105.99$, the number of moles of sodium carbonate in the sample, g the grams of NaCO_3 in the titrated sample, V is the original volume of water in which the sample was dissolved and v is the volume of HCl added to reach the second equivalence point in the titration. Of course in both equations (1) and (2) $[\text{H}^+] = \text{antilog}_{10}(-\text{pH})$. Once K_{a1} is found equation (1) may be used to find K_{a2} .

As a preparation for this experiment review sections 17-6 and 18-4 of the Petrucci, 8th ed.

In preparation for the Acid-Base Buffer experiment, obtain your group number for your assigned pH values from your TA.

Write your Group number here. _____.

**Safety: Remember to always wear gloves when handling all acids and bases
WEAR YOUR GOGGLES!**

Work in pairs throughout this experiment.

Each student must collect data and submit a separate report.

The actual data analyses and the written reports must be done entirely independently of your lab partner or other students. Make sure that you avoid unauthorized collaboration and plagiarism. All suspected violations of the Code of Academic Conduct will be referred to Student Judicial Affairs.

Experimental Procedure

1. For this procedure, you will need approximately 1 g of dry sodium carbonate. This should be dried for at least two hours in the oven in the laboratory room the period before you do this procedure.
2. Accurately weigh 0.15 - 0.25 grams sodium carbonate by difference into each of three marked 100 mL, 150 mL, or 250 mL beakers, recording the exact weight in your lab notebook, e.g. 0.197 g. Handle the sample vial only with a strip of folded paper or with your crucible tongs so that your fingerprints do not produce spurious weighings. Dissolve with 30 mL deionized water, measured with a clean and conditioned buret. Record the volume of water as precisely as possible. Add a few drops of phenolphthalein indicator to each sample. The volume of water in which you dissolve the sodium carbonate is the initial volume of analyte that was symbolized by v in the equations in the introduction. A magnetic stir bar will be used during the titration to continuously stir the solution. The magnetic stir bars function using the stir option on the electric hotplates. Do not heat your sample.
3. Condition your 50 mL buret with a small amount of your standardized HCl solution saved from the experiment on "Strong acid strong base titration curve" and then properly fill the buret.
4. Calibrate the pH meter as described in the instructions provided in the laboratory. Be sure to use both the lowest pH and the highest pH buffer solutions while calibrating because of the large pH range you will need.
5. Assemble a stir plate under the buret clamp nearest the pH meter you are using, put your filled buret into this clamp and put the beaker with the carbonate solution under the buret but atop the stir plate. Rinse off the pH electrode with deionized water, gently wipe the electrode with a Kimwipe and place it into the beaker using a utility clamp to clamp the pH electrode so that it is below the level of the liquid in the beaker, but does not touch the bottom. Position the buret tip inside the mouth of the beaker away with the stopcock in a convenient position to be manipulated. The positioning of all the items is rather close; you will probably have to place the stir bar somewhat displaced from the center of the beaker so that it will not collide with the pH electrode.

6. When the assembly is ready, turn on the magnetic stir bar slowly and increase the setting gradually until you have it rotating at a moderate speed.
7. Titrate your Na_2CO_3 solution with the standardized HCl, taking readings on the pH meter with measured increments of added HCl solution. Do not use your wash bottle to rinse down the sides of the beaker at any time during this titration as the volume of water added during the wash would invalidate the pH readings. The only volume changes that may take place must come from added HCl solution. Add approximately 1 mL of HCl, give the system time to equilibrate and the pH meter time to stabilize, then record the buret reading and the pH in your notebook, leaving a blank column between them to be filled in with the volume of HCl added (present buret reading minus initial buret reading). Take readings for every 1 mL increment until a pH of 9.6 is reached. Then take readings every 0.10 mL (~ 2 drops) until a pH of 7 is reached. During this time, the solution should turn clear. Record the color changes as they occur alongside the buret readings and pH readings so that you have a record of the pH range over which phenolphthalein changes color.
8. Once the solution is clear, add a few drops of bromocresol green. Continue past the first endpoint using 0.1 mL increments until you have added an additional 1 mL of titrant. When you have passed the first endpoint by 1 mL you may increase the increment to 1 mL again. Continue to titrate, reading the pH after each 1 mL increment addition until pH 5.5. Then, take readings every 0.10 mL until the color changes to yellow. Take notes of the color changes alongside your buret readings and pH readings so that you have a record of the pH range over which bromocresol green changes color. Continue taking readings every 0.10 mL until you are 2 mL past the endpoint. Then take readings every 1 mL until another 6 increments of HCl solution have been added.
9. The titration data is most efficiently collected if one partner is adding the HCl and reading the pH meter while the other records the data. When one complete titration is finished, the partner who has been adding the HCl and reading the pH meter will need to copy the recorded data into her own notebook. Be sure to identify the sample and its mass at the top of the page when the titration curve data is copied. You will now repeat the titration for the remaining two samples and should exchange roles if you did not trade off during the first titration. Each partner needs to have performed all roles. You should modify your technique for the remaining two samples based on your experience with the first one. You may find these general directions need to be slightly adjusted to improve the quality of data for your curve, for example by choosing a somewhat different specific pH at which to change the increment sizes.

Data Analysis

1. What are the precise masses of Na_2CO_3 used for each of your three titration curves?
2. Prepare plots of your titration data and of the first and second divided differences as was described in the “Strong acid strong base titration curve” experiment to help you more accurately determine the equivalence point. You may find it convenient to copy and

modify the spreadsheet program you prepared to work up the data for that experiment and use it here. A first divided difference curve is the graph of the change in pH divided by the change in volume ($\Delta\text{pH}/\Delta V$) versus the volume added. It approximates the first derivative (rate of change of pH with volume). A second divided difference curve is the graph of the change in $\Delta\text{pH}/\Delta V$ versus volume or $\Delta\Delta\text{pH}/\Delta V\Delta V$ versus volume. It approximates the second derivative (rate of change of the rate of change). On the first divided difference curve the equivalence point of the titration is the maximum point of the graph, and on the second divided difference curve the equivalence point of the titration is where the graph passes through the horizontal axis. Examples of these plots can be found at the end of the laboratory procedure description for the experiment “Strong acid strong base titration curve”. From these plots, determine the volume of HCl required to reach the equivalence points in your titrations. **Print copies of these plots to turn in to your teaching assistant. Title each graph clearly, label the vertical and horizontal axes, and make sure your name is on each of the graphs.** Using the same sequence in which you ordered the masses of Na_2CO_3 , what are your best values for the volumes of HCl required to reach the first equivalence point in the titration (carbonic acid second proton equivalence point) for each of your three titration curves? Again, in the same sequence, what are your best values for the volumes of HCl required to reach the second equivalence point in the titration (carbonic acid first proton equivalence point)?

3. Over what pH range did phenolphthalein change color? What was the color change?
4. Over what pH range did bromocresol green change color? What was the color change?
5. Using the data for the second equivalence point (the equivalence point of the first proton dissociation from carbonic acid), use equations (2) - (4) of the introduction to this experiment to calculate K_{a1} from each of the three titration curves. What are the three values of K_{a1} that you get from your curves? What is the standard deviation among them?
6. Use the pH of the first equivalence point (the equivalence point of the second proton dissociation from carbonic acid equation (1) of the introduction and the values of K_{a1} you determined in Question 5 to calculate K_{a2} for each of the three titration curves. What are the three values of K_{a2} that you get from your curves? What is the standard deviation among them?

Conclusion After reflecting on the nature of the titration curve for a diprotic acid the difference from that of a monoprotic acid, and the complexity of analyzing the data from the titration curve to extract the values of the acid dissociation constants, compose a few paragraph summary of this experiment. Include some comments about the sources of error in the experiment that may be responsible for the difference between the values you have obtained and the accepted literature values for the dissociation constants of carbonic acid.

