CARBONATE BUFFERS IN NATURAL SOILS AND WATERS

MATERIALS: pH meter; magnetic stirrer and stirbar; standardization buffers (pH=4, 7 and 10); 50 mL buret; 400 mL beaker; 250 mL beaker (4); 50 mL beaker (2); vials (2); 100 mL and 50 mL graduated cylinders; filter funnel and filter paper; disposable cups; anhydrous CaCO3; saturated solution of CaCO3; KCl(s), 0.00216 M H2SO4; simulated acid rain (H2SO4 with pH~4.25), 0.01 M H2SO4 and 0.01 M NaOH in dropper bottles; natural samples of topsoil, peat moss, sand, and limestone.

PURPOSE: The purpose of this experiment is to examine the buffering action of carbonate materials and to relate that to natural buffering against acid rain.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Standardize and use a pH meter.
2. Evaluate experimental data in terms of buffer capacity both qualitatively and quantitatively.
3. Relate experimental measurements to environmental situations.
4. Determine solubility of a sparingly soluble salt from titration data.

DISCUSSION

Although neutral water has pH = 7 at 25ºC, water in rain and some lakes and streams becomes naturally acidified from dissolved CO2, a natural component of the atmosphere. Carbon dioxide reacts reversibly to form the weak polyprotic acid H2CO3, which further ionizes into hydronium and hydrogen carbonate ions.

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

The pH of water in equilibrium with atmospheric CO2 is about 5.6, so natural, unpolluted rainwater is slightly acidic. Any precipitation with pH below 5.6 is considered to be “acid rain” (or “acid deposition” when all forms of precipitation are considered). The primary acidic components of acid rain are H2SO3, H2SO4 and HNO3, formed by the dissolution of gaseous sulfur and nitrogen oxides into raindrops as they fall. (The NO2 and SO2 are produced in combustion of sulfur-containing coal, or by internal combustion engines.) Since H2SO4 and HNO3 are strong acids, they can affect the pH of rain enormously. The average annual pH of precipitation falling in the northeastern US is between 4 and 4.5, but it has been as low as 1.5 in limited instances. This can have serious consequences for both plants and animals.

The chief natural defense against acid rain is a buffer system governed by the equilibrium between carbonic acid and carbonate ions (Eq. 1). In addition, significant natural buffering is associated with the presence of insoluble carbonate salts such as MgCO3 and CaCO3 in natural bedrock. (Limestone, for example, is mostly CaCO3.) The carbonate ions can accept protons from water, and also generate hydrogen carbonate ion.

\[
\text{CaCO}_3 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + \text{CO}_3^{2-} (aq)
\]

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

The summation of reactions 1-3, along with the autoionization equilibrium of water, yields an overall equation that accounts for the formation of hydrogen carbonate ions and the equilibrium between atmospheric CO2 and aqueous ions necessary for acid rain buffering:

\[
\text{CO}_2 (g) + \text{CaCO}_3 (s) + \text{H}_2\text{O} (l) \rightleftharpoons \text{Ca}^{2+} (aq) + 2 \text{HCO}_3^- (aq)
\]

This buffer system is only effective if large amounts of solid carbonate are readily available. Carbonate ions react with the strong acid to produce hydrogen carbonate, a weak acid

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

The additional HCO$_3^-$ subsequently shifts equilibrium (1) to form more CO$_2$ as well. Water systems in areas with large amounts of carbonate present (usually in the form of chalk, marble or shale bedrock) have significant buffer capacity and can withstand large amounts of acid precipitation without a corresponding large decrease in pH.

The term “acid neutralizing capacity” (ANC) is also used to describe buffer capacity in the context of acid rain, since only buffering against strong acid is important for that application. The ANC is expressed in terms of ppm CaCO$_3$ (mg CaCO$_3$/L), even though several different carbonate salts may be responsible for the action. Lakes in areas where the bedrock does not supply carbonate (such as the granitic bedrock of the Canadian Shield) have low buffer capacity (low ANC) and are extremely susceptible to ecological damage caused by acid rain.

In this experiment we will examine the principles of the buffering effect described above, and test some samples for their buffer capacity.

**PROCEDURE (work in groups of four; each pair does all of part A, one segment of Part B, and all of Part C):**

**Part A. Standardization of the pH meter.**

1. Follow the directions of your instructor regarding the operation of the pH meter and care and use of the electrode.

2. Standardize each of the pH meters with the three buffer solutions provided (pH = 4, 7 and 10). It is NOT necessary to pour the buffers out of their vials; simply make the measurements in the original containers.

**Part B. Examination of Carbonate Buffering (two pairs work together; one pair does Segment I, the other does Segment II).**

**Segment I – Saturated CaCO$_3$ solution.**

1. Set up a filter funnel, using a clean 250 mL beaker as a receiver. To ensure that no solids are included in the sample, pour saturated CaCO$_3$ solution through the filter until you have collected about 125 mL in the receiver beaker. Using a graduated cylinder, measure out 100.0 mL of the filtered solution and pour it into another clean 250 mL beaker. Add 0.1 g KCl ionic strength adjuster to help stabilize the meter. Add a stir bar and place the beaker on the magnetic stirrer. Place the pH electrode in the solution and stir gently.

2. Record the actual concentration of the ~0.002 M H$_2$SO$_4$ solution. Rinse the buret with that solution, remove any air bubbles from beneath the stopcock, and refill the buret. Mount the buret in a buret clamp and arrange the buret so that additions of titrant can be made while the pH electrode remains in the solution in the beaker.

3. Record the pH of the solution before any titrant is added. Then, add titrant in 1.00 mL increments, recording the pH when the values stabilize, until 12 mL of titrant have been delivered. **Wait until the pH reading stabilizes before recording the value, or adding more titrant. (NOTE: This might take a few seconds, or several minutes, depending on where you are in the titration.)**

4. After you have added 12 mL of titrant, remove, rinse and secure the pH electrode, retrieve the stir bar and wash all of your glassware, including the buret. Excess solutions can be safely discarded in the sinks.

5. Exchange your Part B data with the group working on Segment II, so that all groups have all the data on all three solutions.

**Segment II – Saturated CaCO$_3$ solution with excess solid, and water.**

1. Set up a filter funnel, using a clean 250 mL beaker as a receiver. Pour saturated CaCO$_3$ solution through the filter until you have collected about 125 mL in the receiver beaker. Using a graduated cylinder, measure out 100.0 mL of the filtered solution and pour it into another clean 250 mL beaker. Add a stir bar and place the beaker on the magnetic stirrer. Place the pH electrode in the solution and stir gently. Now, add about 0.1 g of solid CaCO$_3$ to the beaker and stir using the magnetic stirrer. Add 0.1 g KCl ionic strength adjuster to help stabilize the meter.
2. Record the actual concentration of the ~0.002 M H$_2$SO$_4$ solution. Rinse the buret with that solution, remove any air bubbles from beneath the stopcock, and refill the buret. Mount the buret in a buret clamp and arrange the buret so that additions of titrant can be made while the pH electrode remains in the solution in the beaker.

3. Record the pH of the solution before any titrant is added. Then, add titrant in 1.00 mL increments, recording the pH when the values stabilize, until 12 mL of titrant have been delivered. **Wait until the pH reading stabilizes before recording the value, or adding more titrant.** *(NOTE: This might take a few seconds, or several minutes, depending on where you are in the titration.)*

4. After you have added 12 mL of titrant, remove, rinse and secure the pH electrode, retrieve the stir bar and wash the beaker. You should leave the H$_2$SO$_4$ in the buret.

5. **Thoroughly rinse the graduated cylinder with distilled water to remove any carbonate residue, and then use it to measure out 100.0 mL of distilled water into a clean 250 mL beaker.** Add a stir bar, place the beaker on the magnetic stirrer, place the pH electrode in the solution and stir gently.

6. Add 0.1 g KCl ionic strength adjuster to help stabilize the meter for these dilute solutions. Use dropper bottles of 0.01 M H$_2$SO$_4$ or 0.01 M NaOH to bring the pH to about the same value (± 0.25 pH units) as the starting point of the CaCO$_3$ solution just measured. It should only take a few drops of acid or base to accomplish this.

7. Record the pH of the solution before any titrant is added. Then, add titrant in 1.00 mL increments, recording the pH when the values stabilize, until 12 mL of titrant have been delivered. **Wait until the pH reading stabilizes before recording the value, or adding more titrant.** *(This might take a few seconds, or several minutes, depending on where you are in the titration.)*

8. After you have added 12 mL of titrant, remove, rinse and secure the pH electrode, retrieve the stir bar and wash all of your glassware, including the buret. Excess solutions can be safely discarded in the sinks.

9. Exchange your Part B data with the group working on Segment I, so that all groups have all the data on all three solutions.

Part C. Buffering in Natural Samples. *(Work in groups of four.)*

1. Pour about 140 mL of the simulated acid rain into a clean 250 mL beaker. Check and record the pH; it should be close to 4.25. If necessary, use dropper bottles of 0.01 M H$_2$SO$_4$ or 0.01 M NaOH to bring the pH to 4.25 ± 0.25, recording the final value. It should only take a few drops of acid or base to accomplish this.

2. Weigh out about 10.0 g of topsoil in a disposable cup.

3. Use a graduated cylinder to measure out 50.0 mL of your simulated acid rain. Add the sample to the topsoil in the cup. Stir for a minute, then let the mixture sit for a minute so the solids settle to the bottom of the cup.

4. Prepare a filter funnel as in Part B.

5. Place a clean 50 mL beaker below the funnel, and decant the simulated acid rain from the topsoil sample into the filter, collecting the liquid (called the “effluent”). Collect at least 10-15 mL of the effluent. Transfer the liquid to a clean, dry vial and then measure and record its pH. Be sure to clean the pH electrode well after the measurement. Discard the whole cup with the used topsoil sample and filter in the trash, NOT in the sink. Discard your solution and clean the vial.

6. Repeat steps 2 through 5 with the peat moss sample, the sand sample, and the limestone sample, using a fresh filter paper each time. Discard used materials in the trash.

7. After testing your four samples, clean all of your glassware thoroughly. Clean the pH electrode thoroughly and secure the meter.
DATA ANALYSIS:

1. Use Excel to create a plot of pH vs. volume H₂SO₄ for the three solutions treated in Part B. Plot all three solutions on the same graph. Explain the behavior of the three different samples in terms of buffering capacity (i.e. acid neutralizing capacity).

2. One way to calculate the acid neutralizing capacity (ANC) is to find the number of moles of acid that were required to reach a pH of 5.6 (natural rainwater) and to determine the concentration (in ppm or mg/L) of CaCO₃ that would neutralize that much H₂SO₄. Find the ANC for the CaCO₃ solution (without excess solid CaCO₃), based on your graph from part B.

3. Create a table to report your data from Part C. Qualitatively explain the data in terms of the buffering capacity of the different samples.

QUESTIONS FOR CONSIDERATION:

1. If you watched carefully, you would have noticed that when H₂SO₄ was added to the CaCO₃ solution that contained excess solid CaCO₃, the pH decreased quickly, and then slowly rose to a final value. However, when the same titrant was added to the CaCO₃ solution without excess solid, the pH simply went down until it stabilized. What might explain this difference in behavior? (Think about the equilibria involved!)

2. For the saturated CaCO₃ solution, the S-shaped curve in your data represents the titration curve for the dissolved CO₃²⁻ ion. From the inflection point of the curve, estimate the volume of acid needed to titrate the sample to the equivalence point. Use this to determine the concentration of carbonate in the sample. Compare that to the solubility obtained from the Kₛₚ of CaCO₃.

3. Show that the sum of reactions 1-3 in the Discussion section, plus the autoionization of water (Kₐₚ) equilibrium, gives reaction 4.

4. A buffer system consists of a weak acid and its conjugate base, in significant amounts. In natural water systems that show buffer capacity, what is the weak acid, and what is the weak base?
Complete these questions prior to attending lab.

1. Go to the EPA Acid Rain Program website [http://www3.epa.gov/airmarkets/progress/reports/emissions_reductions.htm](http://www3.epa.gov/airmarkets/progress/reports/emissions_reductions.htm) and select “SO2 Trends”. What is the trend in SO2 emissions for the years represented on the graph? How many tons of SO2 were emitted nationwide in 2013? What is the percent reduction since 1980? Note that you can obtain precise numbers by moving your mouse over objects.

2. Go back to the EPA website, and this time select “SO2 State-by-State”. Which state had the highest emissions in 2014? Which state in the lower 48 states had the lowest in 2014? How much SO2 was generated in Maryland in the last year listed?

3. Go to the National Atmospheric Deposition Program website “Annual Maps by Year” [http://nadp.sws.uiuc.edu/NTN/annualmapsByYear.aspx](http://nadp.sws.uiuc.edu/NTN/annualmapsByYear.aspx)
   a. Select “1990 and then “lab H” Deposition” “PDF.” Display the map. Which regions of the US received the most acidic precipitation? (You can sketch these on the map below).

   ![Map of the United States](image)

   b. Select "2014" and 'Lab pH' 'PDF.' What is the pH range of the sites reported in the region you circled in (a) in 2014? What is the pH range in your home state?

4. Use the Ksp to calculate the concentration of CO3^2- ions in a saturated solution of CaCO3 at 25°C.

5. The solubility of MgCO3 is 0.0106 g/100mL.
   a. What is the solubility in molarity?
   
   b. Using the value in a, what volume in mL of 0.00216 M H2SO4 would be necessary to react with 25.0 mL of the saturated MgCO3 solution?

\[
\text{MgCO}_3 \text{(aq)} + \text{H}_2\text{SO}_4 \text{(aq)} \rightarrow \text{MgSO}_4 \text{(aq)} + \text{CO}_2 \text{(g)} + \text{H}_2\text{O}(l)
\]