## Acid Rain

Acid rain is a topic of much concern in today's world. As carbon dioxide gas, $\mathrm{CO}_{2}$, dissolves in water droplets of unpolluted air, the following reaction occurs:

$$
\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \longleftrightarrow \mathrm{H}_{2} \mathrm{CO}_{3}
$$

$\mathrm{H}_{2} \mathrm{CO}_{3}$ is a weak acid that causes the rain from unpolluted air to be slightly acidic. This source of "acid rain" is not usually considered to be a pollutant, since it is natural and usually does not alter the pH of rain water very much. Oxides of sulfur dissolve in water droplets to cause more serious problems. Sulfur dioxide dissolves to produce sulfurous acid, $\mathrm{H}_{2} \mathrm{SO}_{3}$, by the equation:

$$
\mathrm{SO}_{2}+\mathrm{H}_{2} \mathrm{O} \longleftrightarrow \mathrm{H}_{2} \mathrm{SO}_{3}
$$

This source of sulfur dioxide can occur naturally, as from volcanic gases. More often, however, sulfur dioxide is considered a pollutant, since it is a by-product of fossil-fuel combustion.

The acidity of a solution can be expressed using the pH scale, which ranges from 0 to 14 . Solutions with a pH above 7 are basic, solutions with pH below 7 are acidic, and a neutral solution has a pH of 7. In Part I of this experiment, you will study how the pH of water changes when $\mathrm{CO}_{2}$ is dissolved in water. In Part II, you will study the effect sulfuric acid has on the pH of different water types.

## OBJECTIVES

In this experiment, you will

- use a pH Sensor to measure changes in pH .
- study the effect of dissolved $\mathrm{CO}_{2}$ on the pH of distilled water.
- study the effect of dissolving $\mathrm{H}_{2} \mathrm{SO}_{4}$ in various waters on pH .
- learn why some bodies of water are more vulnerable to acid rain than others.


Figure 1

## MATERIALS

LabPro or CBL 2 interface
TI Graphing Calculator
DataMate program
Vernier pH Sensor
Graphical Analysis or graph paper
$250-\mathrm{mL}$ and $100-\mathrm{mL}$ beaker buffer solution

dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$<br>ring stand and utility clamp<br>straw<br>wash bottle with distilled water water from a lake<br>water from the ocean (optional)

## PROCEDURE

## Part I $\mathbf{C O}_{2}$ and Water

As carbon dioxide gas, $\mathrm{CO}_{2}$, dissolves into water droplets suspended in the atmosphere, it changes the rainwater's pH . Here you will test to see if $\mathrm{CO}_{2}$ will affect the pH of distilled water. The source of $\mathrm{CO}_{2}$ will be your breath.

1. Obtain and wear goggles.
2. Before each use of the pH Sensor, you need to rinse the tip of the sensor thoroughly with distilled water. To do this, hold the pH Sensor above a rinse beaker and use the rinse bottle to thoroughly rinse the sensor tip.
Important: Do not let the pH Sensor dry out. Keep it in a $250-\mathrm{mL}$ beaker with about 100 mL of tap water when not in use. The tip of the sensor is made of glass - it is fragile. Handle with care!
3. Plug the pH Sensor into Channel 1 of the LabPro or CBL 2 interface. Use the link cable to connect the TI Graphing Calculator to the interface. Firmly press in the cable ends.
4. Turn on the calculator and start the DATAMATE program. Press CLEAR to reset the program.
5. Set up the calculator and interface for a pH System.
a. If the calculator displays PH in CH 1 , proceed directly to Step 6. If it does not, continue with this step to set up your sensor manually.
b. Select SETUP from the main screen.
c. Press ENTER to select CH 1.
d. Select PH from the SELECT SENSOR menu.
e. Select OK to return to the main screen.
6. Wash a $250-\mathrm{mL}$ beaker with tap water and dry it with a paper towel. Note: All glassware must be clean in this experiment! Put 100 mL of distilled water into this clean beaker. Using a ring-stand and utility clamp, secure the pH Sensor in the beaker as shown in Figure 1. The tip of the sensor should be down in the distilled water. Swirl the water around the sensor tip briefly. Place a clean straw into the distilled water.
7. Record the pH value displayed on the screen as the initial pH (time 0 ) in Table 1.
8. Begin data collection by selecting START on the calculator. Take a deep breath, then gently blow your breath into the distilled water for as long as possible.
9. When data collection is finished, a graph of $\mathrm{pH} v s$. time will be displayed on the calculator screen. As you move the cursor right or left, the time (X) and $\mathrm{pH}(\mathrm{Y})$ values of each data point are displayed below the graph. In Table 1, record the pH value at 10, 20, 30, 40, 50, $60,70,80$, and 90 seconds.

## Part II Simulating Acid Rain Using $\mathrm{H}_{2} \mathrm{SO}_{4}$

10. Empty the distilled water from the beaker and rinse the pH Sensor thoroughly with distilled water from a rinse bottle. Place the pH Sensor in the storage beaker with tap water.
11. Wash and dry the $250-\mathrm{mL}$ beaker. Fill the beaker with a $50-\mathrm{mL}$ portion of distilled water. Set up the beaker and pH Sensor as shown in Figure 1.
12. Set up the data-collection mode.
a. Select SETUP from the main screen.
b. To select MODE, press $\square$ (the up arrow key) once and press ENTER.
c. Select EVENTS WITH ENTRY from the SELECT MODE menu.
d. Select OK to return to the main screen.
13. Select START to begin taking pH measurements. Monitor the pH readings displayed on the calculator screen. When the readings are stable, press ENTER on the calculator.
14. The calculator will prompt you for the number of drops of acid you added to the beaker. Type " 0 " and press ENTER.
15. Add 1 drop of acid to the beaker. Stir the solution thoroughly after addition. CAUTION: Handle the sulfuric acid with care. It can cause painful burns if it comes in contact with the skin. Avoid spilling it on your skin or clothing.
16. When the readings are stable, press ENTER on the calculator. Enter the total number of drops of acid added to the water in the beaker and press ENTER.
17. Repeat Steps $15-16$, adding 1 drop each time until a total of 10 drops has been added.
18. On the calculator, press to stop data collection. A graph will be displayed with pH along the y -axis and the number of drops added along the x -axis. Move the flashing cursor from point to point and record the pH values in Table 2. When finished, press ENTER to return to the main screen.

## $\mathrm{H}_{2} \mathrm{SO}_{4}$ and Water from the Ocean

19. Repeat Steps $13-18$ using "Ocean Water" in place of distilled water.

## $\mathrm{H}_{2} \mathrm{SO}_{4}$ and Lake Water

20. Repeat Steps $13-18$ using "Lake Water" in place of distilled water.

## $\mathbf{H}_{\mathbf{2}} \mathrm{SO}_{\mathbf{4}}$ and Buffer Solution

21. Repeat Steps $13-18$ using "Buffer Solution" in place of distilled water.
22. Using Graphical Analysis, or by hand, make a plot of pH vs. drops of acid added. Place all four graphs (distilled, ocean, lake, and buffered water) on the same plot.

## DATA

## Part I

| Table 1: Adding $\mathrm{CO}_{2}$ from your breath to water |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Time (s) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | $\Delta \mathrm{pH}$ |  |  |  |  |  |  |  |  |  |
| pH |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

## Part II

| Table 2 |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Drops | pH of this water type |  |  |  |
|  | distilled | ocean | lake | buffer |
| 0 |  |  |  |  |
| 1 |  |  |  |  |
| 2 |  |  |  |  |
| 3 |  |  |  |  |
| 4 |  |  |  |  |
| 5 |  |  |  |  |
| 6 |  |  |  |  |
| 7 |  |  |  |  |
| 8 |  |  |  |  |
| 9 |  |  |  |  |
| 10 |  |  |  |  |
| $\Delta \mathrm{pH}$ |  |  |  |  |

## QUESTIONS

1. Calculate the change in $\mathrm{pH}(\Delta \mathrm{pH})$ for the water in Part I. What conclusion can you make about your breath?
2. Why does the pH change rapidly at first, and remain stable after a time?
3. Calculate the change in $\mathrm{pH}(\Delta \mathrm{pH})$ for each of the Part II trials.
4. Compare the $\Delta \mathrm{pH}$ values. Which test gave the largest pH change? Which test gave the smallest pH change?
5. Water from the ocean is said to be "naturally buffered." From the result of this experiment, what does this mean?
6. How does water from the ocean become buffered?
7. Many aquatic life forms can only survive in water with a narrow range of pH values. In which body of water, lakes or oceans, would living things be more threatened by acid rain? Explain.
8. There are numerous coal-burning electric power plants along the Ohio River in Southern Indiana where the river and lake waters are naturally buffered. However, air pollution produced there is more harmful to water life in Upstate New York where the river and lake waters are NOT buffered like those in Southern Indiana. A similar situation exists in Europe where air pollutants from highly industrialized Germany are more harmful to Scandinavian water life than to water life in Germany. Use the results of this experiment to explain these situations.
9. Summarize your conclusions of this laboratory experiment. Use your data to answer the purposes of this experiment.

## EXTENSIONS

1. Test hard and soft water in the same way you tested lake and ocean water. How do they compare?
2. Do library research to get more information on the effects of acid rain on streams and lakes.
3. Do library research and prepare a report on "naturally buffered" streams and lakes.

## Acid Rain

1. The water in Part I should be boiled, cooled, and stored in a bottle filled to capacity. This will prevent the $\mathrm{CO}_{2}$ from the atmosphere from affecting its pH . Alternatively, you can adjust the pH with 0.050 M NaOH to about 7 . The latter option is much easier to accomplish.
2. To prepare the dilute $(0.02 \mathrm{M}) \mathrm{H}_{2} \mathrm{SO}_{4}$ solution, dilute 1.1 mL of concentrated sulfuric acid into distilled water to make a total volume of 1 L .
3. If ocean water is not available, synthetic ocean water can easily be prepared:

- Dissolve the following ingredients, one at a time in the order given, in 800 mL of distilled water: $23.2 \mathrm{~g} \mathrm{NaCl}, 1.11 \mathrm{~g} \mathrm{CaCl}_{2}, 6.46 \mathrm{~g} \mathrm{MgCl}_{2}$.
- Add 0.84 g of $\mathrm{NaHCO}_{3}$ slowly with rapid stirring.
- Add $5.40 \mathrm{~g} \mathrm{Na}_{2} \mathrm{SO}_{4}$.
- Bring the volume up to 1 L with distilled water.
- Bring the pH of the solution to 7.8 , using 0.01 M NaOH .
- Fill the bottle completely and stopper it tightly. This will prevent the pH from lowering due to the absorption of $\mathrm{CO}_{2}$.

4. If lake water is not available, hard or soft water might be used, depending upon the local water characteristics:

A recipe for hard water follows:

- To 800 mL of distilled water, add $0.12 \mathrm{~g} \mathrm{CaCO}_{3} ; 0.10 \mathrm{~g} \mathrm{CaSO}_{4} ; 0.038 \mathrm{~g} \mathrm{MgCl}_{2}$.
- With rapid stirring, slowly add $0.10 \mathrm{~g} \mathrm{NaHCO}_{3}$.
- Bring the volume up to 1 L with distilled water.

A recipe for softened hard water follows:

- To 800 mL of distilled water, add $0.191 \mathrm{~g} \mathrm{NaCl} ; 0.107 \mathrm{~g} \mathrm{Na}_{2} \mathrm{SO}_{4}$.
- With rapid stirring, slowly add 0.109 g NaHCO 3.
- Bring the volume up to 1 L with distilled water.

5. To prepare a buffer solution, add up to four times the recommended amount of water to a commercially available pH 7 buffer tablet. Since the amount of acid added is very small, the buffer tablet need not be made to full strength.

Vernier Software sells a pH buffer package for preparing buffer solutions with pH values of 4,7 , and 10 (order code PHB, \$10). To prepare a standard solution, simply add the capsule contents to 100 mL of distilled water. This solution can be diluted to 500 mL for this experiment.

You can also prepare a pH 7 buffer using the following recipe: Add 582 mL of 0.1 M NaOH to 1000 mL of 0.1 M potassium dihydrogen phosphate.
6. The pH calibration that is stored in the DataMate program works well for this experiment. For more accurate pH readings, you (or your students) can do a 2-point calibration for each pH system using $\mathrm{pH}-4$ and $\mathrm{pH}-10$ buffers.

## SAMPLE RESULTS

The following data will be different from students' results.
Part I

| Table 1: Adding $\mathrm{CO}_{2}$ from the breath to water. |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Time (s) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | $\Delta \mathrm{pH}$ |
| pH | 6.1 | 5.1 | 4.8 | 4.6 | 4.6 | 4.6 | 4.6 | 1.5 |

Part II
The following data were taken from the Puget Sound area.

| Table 2 |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Drops | pH of this water type |  |  |  |  |
|  | distilled | ocean | lake | buffer |  |
| 0 | 6.5 | 6.4 | 7.2 | 7.1 |  |
| 1 | 4.3 | 6.3 | 6.4 | 7.0 |  |
| 2 | 3.9 | 6.2 | 6.1 | 6.6 |  |
| 3 | 3.7 | 6.2 | 5.8 | 6.4 |  |
| 4 | 3.5 | 6.1 | 5.6 | 6.3 |  |
| 5 | 3.4 | 6.1 | 5.4 | 6.2 |  |
| 6 | 3.4 | 6.0 | 5.3 | 6.1 |  |
| 7 | 3.3 | 6.0 | 5.2 | 6.0 |  |
| 8 | 3.2 | 5.9 | 5.1 | 5.9 |  |
| 9 | 3.2 | 5.9 | 5.0 | 5.8 |  |
| 10 | 3.1 | 5.8 | 5.0 | 5.7 |  |
| $\Delta \mathrm{pH}$ | 3.4 | 0.6 | 2.2 | 1.4 |  |



## ANSWERS TO QUESTIONS

1. Exhaled breath contains carbon dioxide that causes the water to become acidic $-\mathrm{CO}_{2}$ reacts with the water to make carbonic acid, $\mathrm{H}_{2} \mathrm{CO}_{3}$.
2. As the water becomes saturated with $\mathrm{CO}_{2}$, no more $\mathrm{CO}_{2}$ can dissolve in the water. When this happens, no more $\mathrm{H}_{2} \mathrm{CO}_{3}$ is formed, so the pH remains stable.
3. Answers may vary.
4. The distilled water should yield the largest change, followed by lake water, ocean water, and the buffer. The buffer should resist pH changes more than the others.
5. Buffers resist pH changes. As acid is added to the ocean water, the pH changes less than with other natural water sources.
6. The ocean water is buffered due to a mixture of salts. Some of these salts are capable of resisting changes in pH .
7. Living things would be more threatened by acid rain in lake water, as it is not as well buffered as ocean water.
8. Winds may blow polluted air vast distances. Acid rain may affect bodies of water far from the polluted air's origin, especially if the acid rain falls in unbuffered waters.
9. Student answers may vary.

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