Experiment GB-5: Acid Rain

Background

Acid rain is a worldwide environmental problem that occurs when sulfur dioxide (SO_2) and nitric oxide (NO) from industrial emissions enter the atmosphere. These chemicals are transformed into acids when mixed with air and water, and transported by clouds in droplets of water. When these pollutants fall to earth in any form of precipitation or dust, the acidity of soil and water in the environment is increased. When the droplets are moved by the wind, the effects of the pollutants can take place great distances from the source of the pollutants and lead to:

- The increased acidity of lakes to the point that fish and invertebrates can no longer live there anymore.
- The removal of essential minerals from the soil that are needed for plant growth, thus causing damage to crops and destruction of forests.
- The release toxic ions from the soil that contaminate the water supply.

Table GB-5-1: Concentrations and Sources of Substances Causing Acid Rain.

	Substances Causing Rainwater Acidity		
	CO_2	NO	SO_2
Concentration in Clean Air	350 ppm	0.01 ppm	<0.01 ppm
Natural Sources for Each Substance in Clean Air	Decomposition of Organic Matter	Lightning	Volcanos and Biological Decay
Concentration in Polluted Air		0.2 ppm	0.1-2.0 ppm
Sources of Emissions of Each Substance in Polluted Air (USA 2002)		Transportation (54%) Electric Utilities (22%) Fuel Combustion (17%) Industry (5%) Other (2%)	Electric Utilities (67%) Fuel Combustion (19%) Industry (9%) Transportation (5%) Other (1%)

The slight acidity of normal rainwater, about pH5.6, comes from the naturally occurring concentrations of nitric oxide, sulfur dioxide, and carbon dioxide (CO_2) in the lowest layer of the atmosphere. When the concentrations of nitric oxide and sulfur dioxide are altered by the addition of large quantities of these compounds from industrial activities, like the production of electricity using fossil fuels (Table GB-5-1 on page 1), the rainwater becomes more acidic. In some environments around the world, the rainwater is pH3.0, which is about a thousand times more acidic than normal rainwater.

Carbon dioxide comes from the natural decomposition of organic material. It is the most abundant of the three gases and contributes the most to the acidity of clean, unpolluted rainwater by creating carbonic acid when mixed with water. Carbonic acid dissociates in water. The release of hydrogen ions increases the acidity of the water:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$

Nitric oxide is formed naturally during lightning storms through the reaction of the two most common gases in the atmosphere, nitrogen and oxygen. Nitric oxide is oxidized to nitrogen dioxide (NO_2) which reacts with water to yield nitric acid (HNO_3). Nitric acid also dissociates in water and increases its acidity:

$$N_2 + O_2 \rightarrow 2\ NO$$

$$2\ NO + O_2 \rightarrow NO_2$$

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

$$HNO_3 \rightarrow H+ + NO_3^-$$

The relative amount of nitric oxide produced naturally is small when compared to carbon dioxide. However, since nitric oxide forms acid more readily than carbon dioxide, a small increase in nitric oxide can lead to a large change in rainwater acidity. When the nitric oxide in polluted air mixes with water, nitric acid accounts for about 25% of the acidity in polluted rainwater. The majority of nitric oxide released into the atmosphere comes from the high temperature combustion of fuels in vehicles and power plants

Sulfur dioxide is formed naturally from volcanic activity and biological decay. Sulfur from these sources reacts with oxygen in the air to form sulfur dioxide. In turn, the sulfur dioxide reacts with water to produce sulfuric acid. Sulfuric acid is a strong acid that readily dissociates to form hydrogen ions:

$$S + O_2 \rightarrow SO_2$$

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$H_2SO_4 \rightarrow H^+ + HSO4^-$$

$$HSO_4^- \rightarrow H^+ + SO4^{2-}$$

Just like nitric oxide, an increase in concentration of sulfur dioxide in the atmosphere leads to significant increases in the acidity of rainwater. The majority of sulfur dioxide comes from the sulfur released into the atmosphere from the combustion of sulfur-containing fossil fuels. The concentration of sulfur dioxide in polluted air can reach levels that are 200 times greater that its concentration in clean air. Sulfur dioxide is responsible for about 75% of the acidity of polluted rainwater.

Every ecosystem has a level of pollution, and acidity, that it can tolerate called the *critical load*. The critical load is determined by the ability of the ecosystem to neutralize acid precipitation. Sensitive ecosystems have low critical loads, and tolerant ecosystems have high critical loads. Any level of acidity, or pollution, above the critical load leads to environmental damage.

In this experiment, students will generate the gases that create acid rain: carbon dioxide, nitrogen dioxide, and sulfur dioxide. The gases will then be bubbled through water as the acidity of the water is monitored using pH electrode attached to an iWorx 214 data acquisition unit.

Equipment Required

PC Computer
IWX/214 data acquisition unit
USB cable
IWX/214 power supply
ISE-100 combination pH electrode
Magnetic stirrer
Stir bar
Ringstand
Utility clamp
100 ml beakers (4)
500 ml beaker
Test tubes, 20 x 150mm (3)
Test tube rack
Beral pipettes, long (3)
Pasteur pipette and pipette bulb
Culture tubes, 10 x 75mm (3)
pH 4 and pH 7 buffer solutions
1.0N HCl solution
Sodium Bicarbonate ($NaHCO_3$), solid
Sodium Nitrite ($NaNO_2$), solid
Sodium Bisulfite ($NaHSO_3$), solid
Parafilm or plastic wrap
Spatula

IWX/214 Setup

1. Place the IWX/214 on the bench, close to the computer.
2. Check Figure 1-1 in Chapter 1 for the location of the USB port and the power socket on the IWX/214.
3. Use the USB cable to connect the computer to the USB port on the rear panel of the IWX/214.
4. Plug the power supply for the IWX/214 into the electrical outlet. Insert the plug on the end of the power supply cable into the labeled socket on the rear of the IWX/214. Use the power switch to turn on the unit. Confirm that the red power light is on.

Start the Software

1. Click the Windows **Start menu**, move the cursor to **Programs** and then to the **iWorx** folder and select **LabScribe**; or click on the LabScribe **icon** on the Desktop
2. When the program opens, select **Load Group** from the **Settings menu**.
3. From the dialog box, select **AddedLabs.iws**. Click **Load**.
4. Click on the **Settings menu** again and select the **AcidRain** settings file.
5. After a short time, LabScribe will appear on the computer screen as configured by the **AcidRain** settings. Open the **View menu** and select **Voltmeter** to display the current pH level to appear on the **Main window**.

pH Electrode Setup

Plug the DIN connector on the end of the cable of the ISE-100 pH electrode into Channel 4 on the iWorx unit (Figure GB-5-1 on page 2).

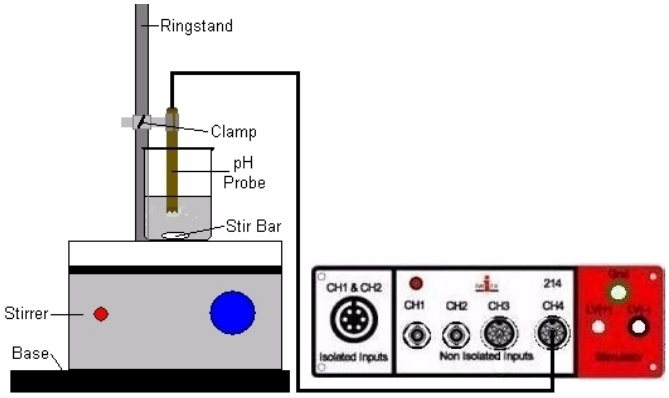

Figure GB-5-1: The arrangement of the stirrer, pH electrode, and beaker for the calibration of the pH probe.

Calibration of the pH Electrode

1. If the pH electrode is still stored in its bottle of buffer, remove the electrode from the bottle. Rinse the electrode with deionized water while holding the electrode over the 500 ml beaker used for the collection of waste liquids.

2 Place the tip of the pH electrode in a 100 ml beaker containing enough room temperature deionized water to submerge the tip. Keep the electrode in deionized water for at least ten minutes.

3 Prepare two 100 ml beakers, each filled with 50 ml of the pH buffers used for calibrating the pH electrode. The buffers should be a room temperature. One beaker is filled with pH 7 buffer; and the other is filled with pH 4 buffer. Each beaker should be filled with enough buffer to cover the tip of the pH electrode, and also allow the stir bar in the beaker to spin without touching the pH electrode.

4 Place the beaker containing the pH 7 buffer on the magnetic stirrer (Figure GB-5-1 on page 2). Carefully place a stir bar in the beaker. Remove the pH electrode from the deionized water and blot any drops of water from the electrode. Position the tip of the electrode in the beaker of pH 7 buffer so that the tip is away from the stir bar. Adjust the speed of the stirrer so the stir bar is rotating evenly at a moderate speed.

5 Click **Start** on the LabScribe **Main window** to begin recording. The trace will eventually reach a stable baseline toward the top of the recording channel. Type the words **Calibration - pH 7** on the comment line to the right of the **Mark button**. Press the **Enter key** on the keyboard to mark the stable baseline of the recording. This comment marks the output of the pH electrode in pH 7 buffer at room temperature. Continue recording while changing the beakers of buffers.

6 Turn off the stirrer and remove the pH electrode from the beaker of pH 7 buffer. Hold the electrode over the beaker used for collecting waste liquid, and rinse it with deionized water from a wash bottle. Blot any drops of water from the electrode.

7 Remove the beaker of pH 7 buffer from the stirrer and place the beaker of pH 4 buffer on the stirrer. Carefully place a stir bar in the beaker. Position the tip of the pH electrode in the beaker of pH 7 buffer so that the tip of the electrode is away from the stir bar. Adjust the speed of the stirrer so the stir bar is rotating evenly at a moderate speed.

8 As you continue to record, the trace will reach a stable baseline toward the bottom of the recording channel. Type the words **Calibration - pH 4** on the comment line to the right of the **Mark button**. Press the **Enter key** on the keyboard to mark the stable baseline of the recording. This comment marks the output of the pH electrode in room temperature pH 4 buffer. Click **Stop** to halt the recording.

9 Select **Save As** in the **File menu**, type a name for the file. Choose a destination on the computer in which to save the file (e.g., a class folder). Click the **Save button** to save the file (as an ***.iwd** file).

10 Turn off the stirrer. Remove the pH electrode from the beaker of pH 4 buffer. Hold the electrode over the beaker used for collecting waste liquid, and rinse it with deionized water from a wash bottle. Blot any drops of water from the electrode and place it in a beaker of deionized water.

Units Conversion

1 Locate the section of the recording where output of the pH electrode was measured in pH 4 and pH 7 buffers. To view this section of the recording in its entirety on the same window, it may be necessary to click either of the **Display Time icons** in the LabScribe **toolbar** (Figure GB-5-2 on page 3).

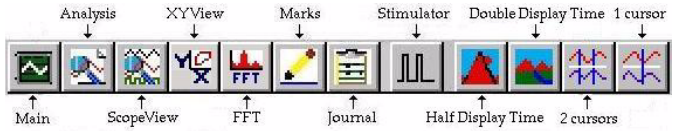

Figure GB-5-2: The LabScribe toolbar.

2 Click the **2-Cursor icon** (Figure GB-5-2 on page 3) so that two blue vertical lines appear over the recording window. Place one cursor on the plateau recorded while the pH probe was in pH 7 buffer. Place the other cursor on the plateau recorded while the pH probe was in pH 4 buffer.

3 **Right-click** on the Channel 4 window to open the **right-click menu**. Select **Units** from the **right-click menu**. Note that the voltage values for the positions of Cursors 1 and 2 are already entered in the **units conversion window**.

- Next to the voltage value for **Cursor1**, enter **7**.
- Next to the voltage value for **Cursor2**, enter **4**.
- Next to the **unit name**, enter **pH**.
- Click **OK**. The units on the Y-axis are equal to **pH** units.

Preparation before Performing Exercises

1 Obtain three culture tubes. These tubes will be used to generate each of the atmospheric pollutants used to treat samples of deionized water.

2 Label each of the three culture tubes with the formula of the solid chemical that it will contain. One culture tube is labeled **$NaHCO_3$**, a second tube is labeled **$NaNO_2$**, and the third tube is labeled **$NaHSO_3$**.

3 Use a spatula to place enough sodium bicarbonate ($NaHCO_3$) in the labeled culture tube to fill the rounded section at the bottom of the tube.

4 Use a spatula to fill the rounded bottom of each of the remaining culture tubes with the corresponding solid chemical, sodium nitrite ($NaNO_2$) or sodium bisulfite ($NaHSO_3$).

5 Cover each of the tubes with parafilm or plastic wrap, and stand them in the test tube rack or in a 100 ml beaker.

Exercise 1: The Effect of Carbon Dioxide on the Acidity of Water.

Aim: To determine the changes in pH that take place in water when carbon dioxide gas is bubbled through the water.

Procedure

1 Place a large test tube with 5 ml of deionized water in the clamp on the ringstand. Remove the pH electrode from the beaker of deionized (DI) water. Blot the drops of DI water from the electrode. Place the electrode in the test tube (Figure GB-5-3 on page 4).

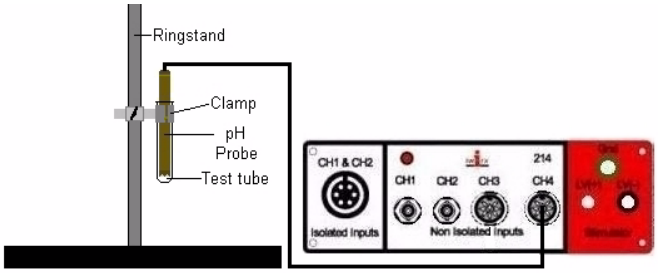

Figure GB-5-3: The arrangement of the test tube and pH electrode for the measurement of the acidity of water treated with atmospheric pollutants.

2 Remove the parafilm or plastic wrap from the top of the culture tube containing $NaHCO_3$. Add 20 drops of 1.0N HCl solution to the tube with a Pasteur pipette. Swirl the culture tube to mix the $NaHCO_3$ and HCl. Cover the tube with the parafilm or plastic wrap. This mixture of chemicals will generate carbon dioxide gas.

3 Click **Start** on the LabScribe **Main window** to begin recording. When the recording on the channel reaches a stable baseline, type **DI Water** on the comment line to the right of the **Mark button**. Press the **Enter key** on the keyboard to mark the recording.

4 Type **CO_2 Added** on the comment line.

5 Obtain a sample of carbon dioxide gas from the culture tube using a long, plastic Beral pipette.

• Squeeze as much air as possible from the bulb of the Beral pipette.

• Insert the tip of the pipette into the culture tube containing carbon dioxide by poking a hole in the parafilm or plastic wrap covering the end of the tube.

Warning: The tip of the pipette should not touch the solution at the bottom of the culture tube.

• Release the bulb of the pipette to draw carbon dioxide gas into the pipette.

6 Insert the stem of the pipette containing the carbon dioxide gas into the test tube holding the water sample and the pH electrode. Lower the stem of the pipette into the tube until the tip of the stem is in the water at the bottom of the tube.

7 Press the **Enter** key on the keyboard to mark the recording as you gently squeeze the bulb of the pipette to bubble carbon dioxide gas through the water. Squeeze as much carbon dioxide gas as possible from pipette. Record for two minutes. If all the gas has been expelled from the pipette before the end of the recording period, remove the pipette from the test tube

Warning: When removing the pipette from the test tube, do not release the pressure on the bulb of the pipette until the tip of the pipette is out of the test tube.

8 Click **Stop** to halt the recording.

9 Select **Save** in the **File menu**.

10 Remove the pH electrode from the test tube. Hold the electrode over the beaker used for collecting waste liquid, and rinse it with deionized water from a wash bottle. Blot any drops of DI water from the electrode and place the electrode in a clean, empty beaker. The electrode will soon be used in the next section of the exercise.

11 Discard the contents of the test tube as directed by your instructor.

12 Obtain a large test tube with 5 ml of deionized water and place it in the clamp on the ringstand. Place the pH electrode in the test tube and proceed to the next exercise.

Exercise 2: The Effect of Nitrogen Dioxide on the Acidity of Water.

Aim: To determine the changes in pH that take place in water when nitrogen dioxide gas is bubbled through the water.

Procedure

1 Remove the parafilm or plastic wrap from the top of culture tube containing $NaNO_2$. Add 20 drops of 1.0N HCl solution to the tube with a Pasteur pipette. Swirl the culture tube to mix the $NaNO_2$ and HCl. Cover the tube with parafilm or plastic wrap. this mixture of chemicals will generate nitrogen dioxide gas.

2 Click **Start** on the LabScribe **Main window** to begin recording. When the recording on the channel reaches a stable baseline, type **DI Water** on the comment line to the right of the **Mark button**. Press the **Enter key** on the keyboard to mark the recording.

3 Type **NO_2 Added** on the comment line.

4 Obtain a sample of nitrogen dioxide gas from the culture tube using the same technique used in Exercise 1.

5 Use the same techniques used in Exercise 1 to add nitrogen dioxide gas to the water sample in the test tube.

6 Press the **Enter** key on the keyboard to mark the recording as you gently squeeze the bulb of the pipette to bubble nitrogen dioxide gas through the water.

Warning: When removing the pipette from the test tube, do not release the pressure on the bulb of the pipette until the tip of the pipette is out of the test tube.

7 Click **Stop** to halt the recording.

8 Select **Save** in the **File menu**.

9 Remove the pH electrode from the test tube. Hold the electrode over the beaker used for collecting waste liquid, and rinse it with deionized water from a wash bottle. Blot any drops of DI water from the electrode and place the electrode in a clean, empty beaker. The electrode will soon be used in the next section of the exercise.

10 Discard the contents of the test tube as directed by your instructor.

11 Obtain a large test tube with 5 ml of deionized water and place it in the clamp on the ringstand. Place the pH electrode in the test tube and proceed to the next exercise.

Exercise 3: The Effect of Sulfur Dioxide on the Acidity of Water.

Aim: To determine the changes in pH that take place in water when sulfur dioxide gas is bubbled through the water.

Procedure

1 Remove the parafilm or plastic wrap from the top of culture tube containing $NaHSO_3$. Add 20 drops of 1.0N HCl solution to the tube with a Pasteur pipette. Swirl the culture tube to mix the $NaHSO_3$ and HCl. Cover the tube with parafilm or plastic wrap. this mixture of chemicals will generate sulfur dioxide gas.

2 Click **Start** on the LabScribe **Main window** to begin recording. When the recording on the channel reaches a stable baseline, type **DI Water** on the comment line to the right of the **Mark button**. Press the **Enter key** on the keyboard to mark the recording.

3 Type **SO_2 Added** on the comment line.

4 Obtain a sample of sulfur dioxide gas from the culture tube using the same technique used in Exercise 1.

5 Use the same techniques used in Exercise 1 to add sulfur dioxide gas to the water sample in the test tube.

6 Press the **Enter** key on the keyboard to mark the recording as you gently squeeze the bulb of the pipette to bubble sulfur dioxide gas through the water.

Warning: When removing the pipette from the test tube, do not release the pressure on the bulb of the pipette until the tip of the pipette is out of the test tube.

7 Click **Stop** to halt the recording.

8 Select **Save** in the **File menu**.

9 Remove the pH electrode from the test tube. Hold the electrode over the beaker used for collecting waste liquid, and rinse it with deionized water from a wash bottle. Blot any drops of DI water from the electrode and place the electrode in beaker of deionized water.

10 Discard the contents of the test tube as directed by your instructor.

Data Analysis

Exercise 1: The Effect of Carbon Dioxide on the Acidity of Water

1 Scroll to the section of data file recorded during Exercise 1.

2 Use the **Display Time icons** on the LabScribe **toolbar** (Figure GB-5-2 on page 3) to position the complete recording from Exercise 1 on the **Main window**.

3 Click on the **2-Cursor icon** in the LabScribe **toolbar** (Figure GB-5-2 on page 3), so that two blue cursors appear over the **Main window**.

4 Select the data to be analyzed by placing a cursor on the pH level recorded before carbon dioxide was bubbled through the water. Place the second cursor on a data point in the recording that is at least two minutes after the initiation of the bubbling of carbon dioxide through the water.

5 Click the **Analysis icon** on the LabScribe **toolbar** (Figure GB-5-2 on page 3) to transfer the data between the cursors to the **Analysis window**.

6 In the table across the top of the data display on the **Analysis window**, the parameters, **Title**, **Value1**, **Value2**, and **V2-V1**, should appear. Any function that does not appear in the table can be selected from the list of functions on the left side of the **Analysis window** by holding down the **Control key** on the keyboard as the name of the function is clicked (**Control-Click**).

7 Once the cursors have been placed in the proper locations for taking measurements, the names and values of these parameters from the data can be recorded in the on-line notebook of LabScribe that is known as the **Journal**. The information can be entered by typing the names and values directly into the **Journal**. The measurements can also be entered into the **Journal** using the functions in the **right-click menu** of the **Analysis window**:

• Place the cursors in the appropriate locations for making measurements.

• Select **Add Title to Journal**, from the **right-click menu**, to add the names of the parameters measured to a table in the **Journal**.

• Select **Add Data to Journal**, from the **right-click menu**, to add the values of the parameters to the **Journal.**

8 In the **Analysis window**, place a cursor on the pH level recorded before carbon dioxide was bubbled through the water. Place the second cursor on a data point in the recording that is at least two minutes after the initiation of the bubbling of carbon dioxide through the water.

9 Select **pH** on the **Value from Ch menu** in the upper left corner of the **Analysis window**.

10 Measure the values for the following parameters from the **pH channel** for the region of data selected:

- **pH-DI Water**, which is **Value1** on the **pH channel**.
- **pH-DI Water and CO_2**, which is **Value2** on the **pH channel.**

11 Record the values for these parameters in the **Journal** using one of the procedures described in Step 7, and on Table GB-5-2 on page 6.

Exercise 2: The Effect of Nitrogen Dioxide on the Acidity of Water

1 Scroll to the section of data file recorded during Exercise 2.

2 Use the same techniques used in Exercise 1 to measure the pH levels of the water before and after nitrogen dioxide was bubbled through the water.

3 Use the same techniques explained in Exercise 1 to record the values of the pH levels in the **Journal**, and in Table GB-5-2 on page 6.

Exercise 3: The Effect of Sulfur Dioxide on the Acidity of Water

1 Scroll to the section of data file recorded during Exercise 3.

2 Use the same techniques used in Exercise 1 to measure the pH levels of the water before and after sulfur dioxide was bubbled through the water.

3 Use the same techniques explained in Exercise 1 to record the values of the pH levels in the **Journal,** and in Table GB-5-2 on page 6

Table GB-5-2: Effect of Atmospheric Pollutants on the Acidity of Water

Gas Added	pH Before Addition	pH After Addition	Change (Δ) in pH
Carbon Dioxide			
Nitrogen Dioxide			
Sulfur Dioxide			

Questions

1 Which gas caused the greatest change in pH when it was added to the water?

2 Which gas caused the smallest change in pH when it was added to water?

3 From the data in this experiment, identify the gas that would cause the pH of unpolluted rainwater to be only slightly acidic.

4 Is the acidity of unpolluted rainwater higher or lower than the acidity of the water measured in this experiment?

5 Is the acidity of highly polluted rainwater higher or lower than the acidity of the water measured in this experiment?

6 Make a list of the items or services that you use each day that contribute to the pollutants that cause acid rain.

7 List some of the solutions for reducing the acidity of natural rainwater.