Unit Overview: Acids in the Environment

This set of three labs introduces the issue of ecosystem acidification. The anthropogenic production of CO$_2$, SO$_x$, and NO$_x$ and subsequent partitioning into water represent a real and continuing threat to many ecosystems. Student will explore the chemistry of these gasses. They will quantify the presence of these pollutants in aqueous systems using titration techniques. Finally they are asked to synthesize this knowledge within the context of ecosystems in a final paper.

The first exercise can be run as a demonstration or as an abbreviated lab. The activity has students make CO$_2$ in a syringe. The CO$_2$ is then introduced into a plastic bag with water samples that contain different amounts of base and an acid/base indicator. The students observe the changes that take place, as the CO$_2$ dissolves into the water to create carbonic acid. In the postlab the students are challenged to think about Henry’s Law and the effect of partial pressure on the partitioning of gasses into water.

The second lab is a classic acid/base titration with an indicator. The students are challenged to find the amount of acid in a water sample. The students must correctly determine the amount of acid in their solution before leaving lab. This lab introduces students to the importance of quantitative analysis. Students will identify and calculate sources of error. They present their findings in a formal lab report which is evaluated and returned to them for revisions.

The final lab in this section challenges students to apply their knowledge of acid/base chemistry to the problem of identifying an unknown acid in solution. In order to differentiate between various acids, the students use potentiometric titration. This allows students to calculate the pKa, and thereby identify the unknown acid. This lab is a great synthesis of acid/base learning goals from lecture, while also introducing a tool relevant to environmental chemistry.
Acid Rain I: Preparation and Properties of Gases

Introduction

Chem Connections

Burning fossil fuels generates many gases. These gases are released into the air. Once in the atmosphere they are able to travel, react, and interact with our environment. In order to understand the impact that an air pollutant has on the environment it is important to consider all of the reactions it can undergo in the environment. During the next few weeks we will be considering how certain pollutants react in the environment to cause acid rain, also how acid rain can cause dramatic changes in aquatic ecosystems.

First we need to consider the interaction of gases with water. All gas molecules can dissolve in water to certain extent. Some of the molecules can react with water to produce acids. The details of this process are explained briefly below.

New Science

The degree to which the gases dissolve in water is expressed by the equilibrium constant $K_H$, sometimes called the Henry’s Law constant. For example, the very important atmospheric gas carbon dioxide dissolves in water. If the system is in sealed, equilibrium is established between the gas and the dissolved gas.

$$\text{CO}_2 (g) \rightleftharpoons \text{CO}_2 (aq)$$

$$K_H = \frac{[\text{CO}_2]}{P_{\text{CO}_2}}$$

For carbon dioxide the Henry’s Law constant is $2.3 \times 10^{-2}$ M·atm$^{-1}$, which is a relatively high value compared to other gases. What this relationship means physically is that the higher the pressure of CO$_2$ gas, the more CO$_2$ will dissolve in the water until the ratio of dissolve gas to gas becomes constant. Part of the reason for the ease of solubility of CO$_2$ is that once dissolved the molecule reacts with water to produce carbonic acid, H$_2$CO$_3$.

$$\text{CO}_2 (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_2\text{CO}_3 (aq)$$

Carbonic acid produces the H$^+$ ion in water, which makes it acidic.

$$\text{H}_2\text{CO}_3 (aq) \rightleftharpoons \text{HCO}_3^- (aq) + \text{H}^+ (aq)$$

$$\text{HCO}_3^- (aq) \rightleftharpoons \text{CO}_3^{2-} (aq) + \text{H}^+ (aq)$$
Acid rain is attributed to a similar set of reactions involving sulfur oxides and nitrogen oxides, collectively referred to as $\text{SO}_x$ and $\text{NO}_x$.

Sulfur Oxides:

$$\text{SO}_2 (g) \rightleftharpoons \text{SO}_2 (aq)$$

$$\text{SO}_2 (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_2\text{SO}_3 (aq)$$

Nitrogen Oxides

$$2 \text{NO} (g) + \text{O}_2 (g) \rightleftharpoons 2 \text{NO}_2 (g)$$

$$\text{NO}_2 (g) \rightleftharpoons \text{NO}_2 (aq)$$

$$\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_3(aq) + \text{HNO}_2(aq)$$

In this experiment you will prepare carbon dioxide gas and observe its effects on water and a basic solution. You will use universal indicator to help to visualize the changes in solution. The indicator changes color with changes in pH.

### Color Changes of a Universal Indicator

<table>
<thead>
<tr>
<th>pH</th>
<th>Universal Indicator Color</th>
<th>Concentration of $\text{H}^+$ (M)</th>
<th>Concentration of $\text{OH}^-$ (M)</th>
<th>Description of Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>Red</td>
<td>$10^{-4}$</td>
<td>$10^{-10}$</td>
<td>acidic</td>
</tr>
<tr>
<td>5.0</td>
<td>Orange-Red</td>
<td>$10^{-5}$</td>
<td>$10^{-9}$</td>
<td>acidic</td>
</tr>
<tr>
<td>6.0</td>
<td>Yellow-Orange</td>
<td>$10^{-6}$</td>
<td>$10^{-8}$</td>
<td>acidic</td>
</tr>
<tr>
<td>7.0</td>
<td>Dark Green</td>
<td>$10^{-7}$</td>
<td>$10^{-7}$</td>
<td>neutral</td>
</tr>
<tr>
<td>8.0</td>
<td>Light Green</td>
<td>$10^{-8}$</td>
<td>$10^{-6}$</td>
<td>basic</td>
</tr>
<tr>
<td>9.0</td>
<td>Blue</td>
<td>$10^{-9}$</td>
<td>$10^{-5}$</td>
<td>basic</td>
</tr>
<tr>
<td>10.0</td>
<td>Reddish-Violet</td>
<td>$10^{-10}$</td>
<td>$10^{-4}$</td>
<td>basic</td>
</tr>
<tr>
<td>11.0</td>
<td>Violet</td>
<td>$10^{-11}$</td>
<td>$10^{-3}$</td>
<td>basic</td>
</tr>
<tr>
<td>12.0</td>
<td>Violet</td>
<td>$10^{-12}$</td>
<td>$10^{-2}$</td>
<td>basic</td>
</tr>
<tr>
<td>13.0</td>
<td>Violet</td>
<td>$10^{-13}$</td>
<td>$10^{-1}$</td>
<td>basic</td>
</tr>
</tbody>
</table>
**Prelab Questions**
Visit the “popular topics” listed on the Environmental Protection Agency website (epa.gov) and read some of the information about acid rain.

1) According to the EPA what are the primary sources of SO$_x$ and NO$_x$ in the United States?

2) What are the natural causes of SO$_x$ and NO$_x$ in the atmosphere? What major natural event in the summer of 2010 might lead to increased levels of SO$_x$ and NO$_x$ in the atmosphere?

3) What is the current atmospheric concentration of carbon dioxide in ppm? Express this value as a partial pressure.

Complete the table below using your textbook or other resources.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Lewis Structure (obeying octet rule)</th>
<th>Lewis Structure (minimizing formal charge)</th>
<th>Henry’s Law Constant, $K_H$ (moles·L$^{-1}$·atm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide, CO$_2$</td>
<td></td>
<td></td>
<td>2.3×10$^{-2}$</td>
</tr>
<tr>
<td>Oxygen, O$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen, N$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur dioxide, SO$_2$</td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>Sulfur trioxide, SO$_3$</td>
<td></td>
<td></td>
<td>infinite</td>
</tr>
<tr>
<td>Nitrogen oxide, NO</td>
<td></td>
<td></td>
<td>1.9×10$^{-3}$</td>
</tr>
<tr>
<td>Nitrogen dioxide, NO$_2$</td>
<td></td>
<td></td>
<td>4.0×10$^{-2}$</td>
</tr>
</tbody>
</table>

4) Which of the gases above is the most soluble in water?

5) Which of the gases above react with water to produce acids?
The Problem
Characterize the effect that CO\textsubscript{2} gas has on solutions which contain base and an indicator.

The Approach
Work with one other person.

**Equipment Needed:**
6 medium test tubes  
1 well plate  
Disposable pipet  
25 mL graduated cylinder  
Parafilm  
Plastic ziplock bag (gallon)  
Stopwatch/timer  
60 mL plastic syringe  
Syringe cap  
Vial cap

**Chemicals Needed:**
0.1 M NaOH Stock Solution  
Deionized water  
Universal indicator  
Sodium bicarbonate, NaHCO\textsubscript{3}, baking soda  
Acetic Acid, CH\textsubscript{3}COOH, vinegar

Making CO\textsubscript{2} gas:
1. Generate a syringe full of CO\textsubscript{2} gas using the instructions list on the following pages.

You will be using serial dilution to obtain 0.01, 0.005, 0.0025, 0.00125, 0.000625, 0.000313 M solutions of NaOH.

2. Dispense a small amount (~3-5mL) of the 0.10M NaOH into a small beaker.
3. Measure out 1 mL of the 0.1 M sodium hydroxide using a plastic pipet and transfer to your first test tube. (Make sure to label all of your test tubes.)
4. Add 9 mL of deionized water to the test tube, cover with parafilm and mix carefully.
5. **Using your pipet, transfer 5 mL of the 0.01 M solution to a new, clean test tube. Add 5 mL deionized water. Mix and repeat using the newly diluted solution until you have six different NaOH solutions in test tubes.**
6. Add 2 drops of universal indicator to each test tube. You should notice a color difference between the solutions.
7. Transfer 2 mL of each solution to the well plate. Fill the four top wells with the solutions.
8. Place a white piece of paper under the well plates, writing the contents of each plate on the area under the plate.
9. Carefully place the well plate inside the plastic bag and remove any excess air. Close the zipper partway, leaving room to inject the CO\(_2\) from the syringe.
10. Place the syringe (about 25%) into the bag. Remove the cap while still in the bag and expel the CO\(_2\) from the syringe into the bag. Remove the syringe and seal the bag as quickly as possible.
11. Start the timer, so that you **record the time as changes occur in the wells.**
12. Fold the bag so that the gas is focused near the well plate.
13. Gently swirl the solutions by carefully agitating the well plate, taking care not to spill the solutions.
14. Record the color changes that occur in each well along with the time. (These should be recorded in your lab notebook, using a table similar to the one shown below.)
15. Universal indicator turns green at a pH of 7. Note how long it takes each solution to turn green.
16. After approximately five minutes, remove the well plate from the bag.
17. Remove the parafilm and note any observations in Table 1.

Table 1: Observations

<table>
<thead>
<tr>
<th></th>
<th>0.01 M NaOH</th>
<th>0.005 M NaOH</th>
<th>0.0025 M NaOH</th>
<th>0.00125 M NaOH</th>
<th>0.000625 M NaOH</th>
<th>0.000313 M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Initial color of solution in test tubes)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color changes and times (example: blue – green at 3 min 12 sec)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Record each change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final Color of the solutions after they have reached equilibrium (~10 min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final pH of the solution (use table on second page of this lab handout)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The following procedure was adapted with permission from *Microscale Gas Chemistry*, Educational Innovations, copyright Bruce Mattson, 2003

**THE IN-SYRINGE METHOD FOR PREPARING GAS SAMPLES**  
**PREPARATION OF CARBON DIOXIDE**

**General Safety Precautions**
Always wear safety glasses. Gases in syringes may be under pressure and could spray liquid chemicals. Follow the instructions and only use the quantities suggested.

**Toxicity**
Carbon dioxide is a relatively non-toxic gas. Like all gases other than oxygen, it is a simple asphyxiant if inhaled in very large quantities. We will not be generating very large quantities of carbon dioxide.

**GETTING STARTED**
Before we start making gases, we need to know a bit more about the equipment that we will use. Many of the important pieces that we will use are pictured below. Let’s start with the most dramatic, the large syringe which may invoke pangs of fear and memories of visits to the doctor’s office. There are no needles, however. You will notice that after working with these syringes a few times, you will no longer think of them for their medical applications. (Incidentally, these 60 mL syringes are used by veterinarians to treat large farm animals and are not normally used by medical doctors.)

The syringe is composed for two major parts — the barrel (outside part) and the plunger (inside part). Plungers and barrels are interchangeable. On one end of the plunger you will notice an air-tight
black rubber seal. Even tiny little hydrogen molecules have trouble sneaking past the seal so these are pretty impressive pieces of equipment.

The next pieces of equipment to find are the two syringe caps. They are made of rubber and fit snugly onto the syringe barrel — again, an air-tight fit. They are tiny and easily lost, which would be a problem because they are used to keep the gas in the syringe. Keep an eye on them and don’t lose them down the drain.

The vial cap is used to lower the solid reagent into the syringe (as discussed below) and is also small and easily lost. Again, you should have two of them. The other items in your gas kit will include a long and short piece of tubing, two weighing dishes, a bottle of silicone oil, a plastic pipet, a plastic cup, two test tubes (two different sizes) and a birthday candle.

**MAKING CARBON DIOXIDE**

You are now about to prepare your first gas sample using the syringe equipment. The general strategy of the method is to react two substances in a large syringe. The limiting reagent is always used in solid form and is placed in a small vial cap. The second reagent is prepared as an aqueous solution. For example, you will generate CO$_2$(g) from vinegar, used in excess, and solid baking soda or sodium bicarbonate, NaHCO$_3$. The steps given below eventually will be used to make all sorts of gases.

1. **Wear your safety glasses!**

2. **Lubricate the seal**
   
   Lubricate the black rubber seal of the plunger with silicone oil.

3. **Measure out the solid reagent**
   
   (Use 0.21 g NaHCO$_3$ to make CO$_2$)
   
   Place the solid reagent into the vial cap. We recommend that the solid be measured directly into the vial cap to prevent losses from transferring small amounts of solids.

4. **Fill the syringe barrel with water**
   
   Fill the barrel with water. Place your finger over the hole to form a seal. Fill completely to the top.
5. Float the vial cap
Float the vial cap containing the solid reagent on the water surface. This is easiest if the syringe barrel is filled completely to the top with water.

6. Lower the cap by flotation
Release the seal made by finger to lower the cap into the syringe barrel without spilling its contents. Allow the syringe to drain into a wide mouth beverage container. When successfully completed, the cap should rest upright on the bottom of the syringe with all reagent still in the cap.

7. Install the plunger
Install the plunger while maintaining the syringe in a vertical position. The plunger should fit snugly against the rim of the vial cap. Push it all the way down. We don’t want more residual air space.

8. Draw aqueous reagent into syringe
(Use 5 mL vinegar to make CO₂)
The aqueous reagent, measured into a small weighing dish, is drawn into the syringe while maintaining the vertical position of the syringe. The vial cap with the solid reagent should float on the solution. DO NOT suck in extra air, this will decrease the partial pressure of CO₂ after the reaction is complete.

9. Install syringe cap
Put the syringe cap on by twisting the cap into the threads of the syringe.
10. Generate the gas
Shake the syringe in order to mix the reagents. As the liquid reagent splashes into the vial cap, gas generation will commence and the syringe plunger should move outward. It is sometimes necessary to gently help the plunger move up the barrel.

11. Remove cap to stop gas collection
After the plunger has reached the desired mark (usually 50 mL), tip the syringe so that it is positioned with plunger downward and syringe cap upward. Carefully remove the syringe cap assuming that the syringe may be under positive pressure. (“Burp that baby with its head up!”)

12. Discharge reagents
Turn the syringe 180° and discharge the liquid reagent into the plastic cup. Caution: Never remove the syringe cap with the cap end of the syringe directed downward: Reagents will spray out of the syringe. Immediately cap the syringe with the syringe cap to prevent loss of gas by effusion.
13. Wash away contaminants

The gas-filled syringe may be "washed" in order to remove traces of unwanted chemicals from the inside surfaces of the syringe before the gas is used in experiments. To wash a gas:

1. Remove the syringe cap,
2. draw 5 mL water into the syringe,
3. cap the syringe,
4. shake syringe to wash inside surfaces,
5. remove cap,
6. discharge water only, and finally
7. recap the syringe.
8. Repeat?

Repeat these washing steps if necessary. (All traces of the reactants should be washed away.)

<table>
<thead>
<tr>
<th>INCORRECT WAY</th>
<th>CORRECT WAY</th>
</tr>
</thead>
</table>

**OTHER USEFUL GAS SYRINGE TECHNIQUES**

There are several other techniques that come in handy when working with gases in syringes. Here are the most important ones. Try to use these techniques as much as possible.

**A. Controlled discharge of gas from a syringe**

Plungers do not always move smoothly in their syringe barrels. As a result, gases may be discharged in large unintended portions (such as 40 mL all at once) if the method shown in the left diagram below is used. Instead, grasp the syringe by its plunger (right figure) and pull the barrel towards your hand. This simple technique will give you excellent control of gas delivery.
C. Discharging a specific volume of gas

Position thumb as a “stop” to discharge desired volume of gas and then push inward.

D. Safety First! Cap Up-and-Off!

If more than 60 mL gas is going to be generated, follow these steps.

1. Position the syringe so the cap is directed upward.
2. Remove the cap by twisting.
3. Discharge the solution to prevent further gas collection. Recap syringe.

Clean-up and storage

At the end of the experiments, clean the syringe parts, caps and tubing with soap and water. Use plenty of soap to remove oil from the rubber seal. This extends the life of the plunger. It may be necessary to use a 3 cm diameter brush to clean the inside of the barrel. Rinse all parts with distilled water. Be careful with the small parts because they can easily be lost down the drain. Important: Store plunger out of barrel unless both are completely dry.

Disposal

Unwanted CO$_2$(g) samples can be safely discharged into the room.
Postlab Discussion Questions

Answer these questions with your lab mates. Write the answers in your lab notebook and turn them in to your GSI at the end of the session. Answering these questions will serve as a good review of concepts for the exam.

1) The lab experiment instructs you to react 0.21g of NaHCO₃ with excess CH₃COOH. How much CO₂ (g) in mL would this reaction generate if all the sodium bicarbonate reacts fully?

2) Using the data that you collected plot the time that it took for each well to turn green. Use concentration of NaOH in the well on the y-axis and time to green on the x-axis. What trends do you notice? (Note: all wells may not turn green.)

3) In lecture you have observed a demonstration using a light bulb to detect the presence of ions in solution. What would you predict for the light bulb experiment for each of the wells?

4) Predict what would happen if you changed the following parameters:
   a. Inject half the amount of CO₂.
   b. Inject the same amount of CO₂ and an equal volume of air.
   c. Inject twice the amount of CO₂.
If there is time, feel free to test out your predictions.

5) Calcium carbonate is a very insoluble salt. If you added a few drops of 0.1M CaCl₂ (aq) to the wells, what would you expect to see? How would the observations differ between the wells?

6) Explain why the different concentrations of NaOH in each of the wells take different times to react with the CO₂.

7) Draw the Lewis structures of CO₂, H₂CO₃, HCO₃⁻ and CO₃²⁻. Rank these in order of increasing attraction to water molecules. Explain your choice. What evidence do you have that supports your predictions?

Bibliography

The procedures for making CO₂ in a syringe were taken with permission from Microscale Gas Chemistry, Educational Innovations, copyright Bruce Mattson, 2003
Acids and the Environment Part II: Determining Molarity

Introduction

Chem-Connections
As we saw in the last experiment, atmospheric carbon dioxide can dissolve in water to produce carbonic acid. Many plant and animal species have evolved to live in very specific chemical environments. For aquatic species this means they can only live within a narrow pH range. Coral reefs are a dramatic example of this pH sensitivity. As the concentration of CO$_2$ in the atmosphere increases, the oceans become more acidic which makes it harder for coral to produce its calcium carbonate exoskeleton. The additional stress of rising temperatures has lead to a massive decline in coral reef growth. Some scientists estimate that by the year 2050 95% of the living coral in the Great Barrier Reef will have been killed, by these relatively small changes in pH and temperature$^1$.

In this experiment you will be titrating a sample of acidic water to determine its concentration. Titrations allow chemists to use concepts like stoichiometry, molar mass and balanced chemical equations to determine the number of moles of reactants being used in a given reaction. These methods and techniques are the scientific basis for quantifying how acidic the oceans may get when CO$_2$ levels in the atmosphere are increased. Using a few relatively simple measurements, scientist can make predictions like the one above.

New Science
The concentration of acidic and basic solutions can be quantitatively determined using a titration. In the titration of acid with base, base is added in increments until the solution becomes neutralized. To visually see the end of the titration, an acid-base indicator is often used. In this experiment the indicator used will thymol blue which changes from yellow to blue as the pH increases from 8 to 10. The primary reaction taking place is the neutralization of the acid with the base. Once the acid is neutralized by the added base, a tiny amount of excess base will start titrating the indicator itself. The color change that results from titrating the indicator signals that the titration has reached the endpoint. When half the molecules of thymol blue indicator are in the basic form (blue) and half are in the acidic form (yellow) the solution is a green color. A blue solution results when too much base is added.

The concentration of the acidic solution can be determined from the titration.

The reaction between the strong base and the acid is:

$$\text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq) \rightarrow 2\text{H}_2\text{O (l)}$$

As soon as \( \text{OH}^- \) is added past the equivalence point the indicator starts to get titrated resulting in a color change. The thymol blue indicator is a diprotic acid that we can represent as \( \text{HInd}^- \), where \( \text{Ind} \) denotes that the acid is an indicator.

\[
\text{OH}^- (\text{aq}) + \text{HInd}^- (\text{aq}) \rightarrow \text{H}_2\text{O} (\ell) + \text{Ind}^{2-} (\text{aq})
\]

yellow \hspace{2cm} blue

If you can, successfully stop the titration at a green color.

**Some new units and calculations:**

Concentration can be expressed in many ways: part per million, percent, molarity, etc. Molarity (M) is defined as moles of solute per liter of solvent (mol/L). For example, a sodium hydroxide solution with a concentration of 2.0 M contains 2 moles of NaOH per liter of water. To find the number of moles in a given volume of solution, just multiply by the concentration.

\[
\text{moles solute} = V_{\text{solution}} \times M_{\text{solution}}
\]

(1)

**Dilutions:**

The initial molarity and volume can be used to calculate the new concentration of a solution that has been diluted. When you dilute something, you do not change the number of moles of material. Many of us have made orange juice from frozen concentrate. Juice is usually made by using one can of concentrate plus three cans of water. The diluted juice is four times less concentrated than the original. The moles of orange juice have not changed, but are instead spread out over a larger volume of water. In the lab, we can use a similar logic.

\[
\text{moles of concentrated solution} = \text{moles of dilute solution}
\]

By substituting Equation 1 you get a more useful relationship,

\[
M_{\text{concentrated}} \times V_{\text{concentrated}} = M_{\text{dilute}} \times V_{\text{dilute}}
\]

(2)

or

\[
M_c \times V_c = M_d \times V_d
\]

**Titrations:**

The volume of NaOH solution required to reach the endpoint of this titration can be related to the moles of acid in your unknown solution. To avoid errors, be sure that the volume of acid is in liters!

\[
\text{moles base} = (V_{\text{base}}) \times (M_{\text{base}})
\]

(3)

If you stop titrating when the solution turns light pink, you have reached the end point successfully so the moles of acid are equal to the moles of the base.

\[
\text{moles acid} = \text{moles base}
\]

(4)

Equations 3 and 4 can be combined to solve for the concentration of the unknown acid solution.

\[
M_{\text{acid}} = (M_{\text{base}} \times V_{\text{base}}) \div V_{\text{acid}}
\]

(5)
Accuracy, Precision and Percent Difference

Often times, when performing a series of replicate measurements, it is useful to determine the precision of those measurements. High precision means that the technique is consistently performed. High accuracy means that the technique yields data that is close to the true value. When performing quantitative measurements, like a titration, analytical chemists strive for high precision and accuracy.

Accuracy and Precision

In this experiment, you will not know how accurate your titration is because you do not know the true value for the molarity of your unknown acid solution. You can, however, determine if your skills at titrating are consistent from trial to trial by calculating a percent difference. Determine the mean of all the “good” titrations, ones where you stopped at the green endpoint. Percent difference can be calculated by comparing each trial to the mean according to the equation listed below. If each trial is close to the mean, that means that each of your titrations were performed consistently.

\[
\text{\% difference} = \left( \frac{|X - \text{mean}|}{\text{mean}} \right) \times 100
\]  

You will be graded on both accuracy and precision in this experiment. This means that you will be evaluated on both the quality and the consistency of your titration technique.
Proper Use of a Pipette

1. Fill pipet by suction to above calibration mark.

2. Remove bulb and immediately cover stem with your dry, right index finger.

3. Wipe off lower stem and tip.

4. Adjust level of meniscus to calibration mark.

5. Drain freely into receiver. Touch pipet to side of container to transfer all of the calibrated volume.

6. The pipet is calibrated to retain a small amount of liquid. Never blow out the remaining amount.

Pipette Details

- Rubber bulb
- Index finger
- Meniscus
- Volume mark
- Liquid that remains
Making a Dilution

1. Dispense a known amount of concentrated solution from a buret into a clean volumetric flask.

2. Using a wash bottle, rinse the neck of the flask with distilled water.

3. Fill Flask $\frac{1}{2}$ full with distilled water and swirl to mix.

4. Dilute the solution until the meniscus is level with the etched line on the neck of the flask.

5. Stopper the flask and turn end over end several times to mix.
Titrination Apparatus

- Buret clamp
- Buret
- Ring stand

Reading a Buret

- Meniscus
- Buret markings
- 3 x 5 card
- Black mark

Buret Reading: 34.73 mL

Titration Technique

- White paper

Experimental

The Problem
Your objective is to perform a series of titrations to determine the concentration of a solution of your unknown acid to three decimal places. During the experiment, you will be learning good analytical techniques as well as gaining an introduction to acid and base reactions and stoichiometry.

The Approach
Work individually, but share the dilute NaOH solution among 2-3 people. Obtain the following items from your lab instructor.

- ~20 mL of 5 M sodium hydroxide (dispense into a small clean, dry beaker.)
- 250.00 mL volumetric flask
- ~40 mL of your unknown acid solution (dispense into a small clean, dry beaker.)

1. Note your unknown number in your lab notebook.
2. Rinse a clean 5.00 mL pipette with a small amount of the 5 M NaOH solution two times. To rinse the pipette, draw up a small amount of solution, tilt to wet the sides, and then drain into a waste beaker. Your lab instructor will demonstrate good pipette technique.

3. Dispense ~15-20 mL of the 5 M NaOH solution into a clean, dry 50 mL beaker. Draw up 5 M NaOH into the pipette until the fluid level is a little bit past the line. Remove the bulb and place your index finger over the top of the pipette. Drain the NaOH to the 5.00 mL mark by slowly lifting your finger. Dispense the 5.00 mL of 5 M NaOH into a clean 250.00 mL volumetric flask. Fill the flask about half way with distilled water and swirl the acid/water mixture. Continue adding water until the meniscus level exactly reaches the line on the flask.

4. Rinse your buret twice with ~5 mL of the diluted NaOH solution. Rinsing should involve wetting the sides of the buret with the NaOH and then draining out the NaOH into a beaker designated for waste. Fill the buret to the top, between 0.00 and 1.00 mL. Record the initial volume to the nearest 0.01 mL in your lab notebook. Burets can and should be read to two decimal places.

5. Rinse your pipette with deionized water thoroughly.

6. Rinse a clean 5.00 mL pipette with a small amount of the unknown acid solution two times. To rinse the pipette, draw up a small amount of solution, tilt to wet the sides, and then drain into a waste beaker. Your lab instructor will demonstrate good pipette technique.

7. Using your pipette, dispense 5.00 mL of your unknown acid into a clean Erlenmeyer flask.

8. Using your wash bottle filled with distilled water, carefully wash all the unknown from the sides of the flask. Add enough water so that the final solution volume is about 25mL.
9. Add 4-6 drops of thymol blue indicator. Note the color of the solution.

10. Add NaOH quickly and slow down as you notice the green color. As you see the appearance of a blue color add base by the drop or half drop. Stop the titration at a green solution, before the solution turns blue. Your lab instructor will display the correct color of the solution at the end point. If you have successfully reached the green endpoint, stop the titration. Record the final buret reading to the nearest 0.01 mL in your lab notebook. Save this solution as a source of comparison for your other trials.

11. Calculate the volume of NaOH used by subtracting the initial volume from the final volume.

12. Calculate the exact molarity of your unknown acid solution to 4 significant figures.

13. Repeat the titration until you obtain three good trials with less than 4% difference between trials. You must compare the molarity of your unknown acid calculated for each trial to the mean molarity. For percent difference calculations, see the calculation section.

Empty all chemical waste in the white five gallon NRC buckets.

Questions and topics to consider for your formal lab report.

Environmental and forensic chemists spend much of their careers determining the amounts of unknown chemicals in complex mixtures. Titrations are a valuable way to make these determinations. Since important decisions will be made on the basis of these measurements it is of the utmost importance that these scientists are confident in their answers.

1) For today’s post lab clearly outline all of your measurements (including volume, weight, and the titration) and identify the error in each one. For example, measurements made on an analytical balance are often accurate to ± 0.0001 g. What is your largest source of error?

2) Use the average value of the acid concentration in the unknown solution to calculate a standard deviation value ($s_N$) for your measurement.

$$s_N = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \bar{x})^2}.$$  

Compare your $s_N$ to the largest source of error in your measurements. Which is a larger value? What does this mean for the accuracy of your experiment?

3) Was your titration successful? How can you tell?

4) Titration with an indicator is a common technique that chemists use when counting moles. Would this technique be useful for determining the pH of a water sample from a lake or stream?

5) Can this technique determine if a lake or stream is affected by acid rain?

6) Given what you learned from the previous exploration of the properties of carbon dioxide, how might this affect the accurate measurement of acid concentration in a natural sample?
Formal Lab Write-Ups:

For the experiments Acid Rain II: Determination of the Molarity and Biofuels Combustion you will complete a full formal lab report. The lab report will follow the format of a scientific journal article and therefore should be typed with diagrams, tables, plots, and equations incorporated within the text. Even though students might share data, each student should write their own report. Plagiarism and cheating will not be tolerated. Formal lab reports are worth 16 points total: 2 points for the prelab exercises and 16 points for the report. In these reports, each section will be scored according to the criteria below.

**Abstract (2 points):**
The abstract is a one paragraph summary of the experiment which outlines the reason for carrying out the experiment and the important results.
- The overall goal is stated correctly, succinctly, and in the student’s own words.
- The general approach to the experiment is described.
- The important results are summarized.

**Introduction (3 points):**
The introduction should provide background information on the experiment, the motivation for its being carried out, a hypothesis of the result, and a justification for the methods used.
- What experiment is being performed?
- Why is the experiment being performed?
- What will the data show?
- The section describes the theoretical basis by which the method is suitable for attaining the goals of the experiment.

**Methods (2 points):**
The method section is a brief description of the experimental procedure, but not a list of steps.
- The important aspects of the experimental method are presented.
- The relevant equipment and techniques are described.
- The laboratory manual is cited as a reference.

**Results (3 points):**
A discussion of the important results obtained in the experiment and the trends observed should be reported. Are the results in agreement with the hypothesis?
- All relevant data and results are presented and clearly labeled.
- Important features or trends are noted in the text.
- Calculations are connected to the method, theory and goals of the experiment.
- Sample calculations are shown.
- Calculations are complete and correct.

**Discussion and Conclusions (3 points):**
The section synthesizes, analyzes and interprets the results of the experiment.
- Results are thoroughly compared with purpose, expectations or theoretical calculations.
- Relevant discrepancies and errors are explained.
- Each error mentioned includes a discussion about the effect on the final values.
- The report demonstrates an understanding of the chemistry and purpose of the experiment.
- Future improvements are proposed.

**Organization, Quality of Writing, Grammar, etc. (3 points)**
The report tells a cohesive story with ideas supported by data.
- Data is logically organized (in tables if appropriate), labeled, and summarized in the text.
- All graphs and plots are logically organized, labeled, and summarized in the text.
- The lab notebook carbon copies are provided for reference.
- Report does not have spelling and grammatical errors.
- Appropriate verb tense is used for each section.
Acid Rain III: Potentiometric Titration

Introduction

Chem-Connections
In experiment 4 you were able to use an indicator titration to determine the amount of acid in an unknown sample. At the end of this analysis you knew how much acid, but you could not identify the source of the acid. In many situations, the chemical identity is as important as the amount of the chemical in solution. This week’s lab introduces a more advanced titration technique, which allows you to simultaneously identify both the amount and type of acid in solution.

In this experiment, you will be given a sample of acid or base relevant to the topic of acid rain. You will titrate it using a solution of known concentration and a pH meter. You will construct a titration curve and share your data with the rest of the class. Each lab pair will have a different solution or a different concentration to investigate so the whole class will benefit from the wide variety of acids studied.

This is a list of acids that will be studied in the experiment. Try to identify the acidic protons from the structures provided.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structure</th>
<th>$K_a1$</th>
<th>$K_a2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric Acid, HCl</td>
<td></td>
<td>very large</td>
<td></td>
</tr>
<tr>
<td>Nitric Acid, HNO₃</td>
<td></td>
<td>very large</td>
<td></td>
</tr>
<tr>
<td>Nitrous Acid, HNO₂</td>
<td></td>
<td>7.1×10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>Sulfuric Acid, H₂SO₄</td>
<td></td>
<td>very large</td>
<td>1.02×10²</td>
</tr>
<tr>
<td>Sulfurous Acid, H₂SO₃</td>
<td></td>
<td>1.23×10⁻²</td>
<td>6.6×10⁻⁸</td>
</tr>
<tr>
<td>Carbonic Acid, H₂CO₃</td>
<td></td>
<td>4.45×10⁻⁷</td>
<td>4.69×10¹¹</td>
</tr>
</tbody>
</table>

The basic techniques that will be used in this experiment are titration and the use of a pH meter. Your instructor will cover these topics in the discussion period.
New Science
A complete discussion of the theory of acid/base titrations, buffers, and pH is given in your textbook. A short summary of the information found within a titration curve is given below.

![Titration of a Weak Acid with Strong Base](image)

1) **Start** - Solution is just an acid in water since no base has been added.
   \[ HA + H_2O \rightleftharpoons A^- + H_3O^+ \]
The pH depends on the strength of the acid and its concentration.

2) **Before equivalence** - A buffer exists, a mixture of HA and A\(^-\) because HA is only partly neutralized by base.
   \[ HA + OH^- \rightleftharpoons A^- + H_2O \]
   \[ pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \]
When exactly half of the acid has been neutralized, the pH reading gives you a very important piece of information. What is so special about the pH at \( \frac{1}{2} \) equivalence?

3) **At equivalence** - HA and OH\(^-\) react completely to give only A\(^-\) in solution. The pH of this solution depends on the chemical properties of A\(^-\). Often A\(^-\) is a weak base so the reaction of a weak base with the water must be considered.

4) **After equivalence** - The is pH dominated by the excess of the strong base added.

**Challenge:** What would the curve look like for the titration of a weak base with a strong acid? How would you predict the pH of the buffer regions?
Experimental

Exploration of Acid Properties Using a Potentiometric Titration

The Problem
Titrates an acid (or base) using standardized NaOH (or HCl) solution and a pH meter to construct a titration curve. Share data with the class to better understand the chemistry of a wide variety of acids.

The Approach
Work in groups of 2-4 depending on the availability of pH meters in your lab room.

Equipment needed:
• solution (record the name and concentration!)
• pH meter
• buret
• standardized NaOH solution (record the exact molarity!)
• standardized HCl solution (record the exact molarity!)

1. Record the identity and concentration of your solution in your lab notebook.

2. Obtain and calibrate a pH meter following the instructions given in the Appendix.
   Please be careful with the pH electrodes because they are expensive and fragile. The pH probes should be stored in a pH4 buffer solution when not in use. Instructions for the use of the pH meter are given in the appendix of this lab manual. Put the meter in “Read Mode” during your titration experiment.

3. To get accurate and quick pH readings, be sure to swirl the solution. This helps to
mix the solution and brings solution to the probe tip.

4. Dispense approximately 150 mL of your solution into a clean, dry beaker.

5. Using a clean, dry graduated cylinder, transfer 50.0 mL of your solution into a clean, dry 250 mL beaker. Why should the glassware be clean and dry?

6. Rinse your buret twice with a few mL of the standardized NaOH solution. (Note: if you are titrating a base you will fill the buret with the HCl solution.) Fill the buret to some point between 0 and 1 mL. Record the initial volume to the nearest 0.01 mL in your lab notebook. Burets can and should be read to two decimal places. For this experiment, it is easiest to start with your buret at 0.00 mL. Why?

7. Place the pH meter into the beaker and perform a “rough” titration by adding NaOH approximately 1 mL at a time from your buret and recording the volume added and pH at each interval. Make a rough plot of the pH as a function of volume of NaOH added in your lab notebook. If your initial buret reading was not 0.00 mL, you will need to subtract the initial reading from all of your buret readings. Continue the titration until you see a sharp rise in the pH at the equivalence point followed by a leveling off in the region following the equivalence point.

8. Record the approximate mL of standardized NaOH (or HCl) it required to reach the equivalence point.

9. Now perform a more accurate titration, this time recording more data points around the equivalence region by adding smaller amounts of base. Repeat steps 1-5 and begin the accurate titration.

10. When you reach a total volume within 2.0 mL of your equivalence point reduce the size of the additions to approximately 0.1 mL intervals and continue until you are approximately 1.0 mL past the equivalence point(s).

11. Continue titrating using 0.5 mL intervals until you have reached a point 3.0 mL past the equivalence point, or have run out of standardized NaOH in your buret.

12. Construct a titration curve (pH vs. V base added) in your lab notebook or using a graphing program such as Excel. Instructions for the use of Excel can be found in the Appendix. This data is not linear, so you do not need to fit the data to a linear model.

13. Share your data with the class. Using the large graph paper sheets provided, draw a plot of pH as a function of mL of NaOH added. Label the pH and volume at the following points: initial, half equivalence, equivalence, and final. As a class, you will use this data to determine trends in acid and base behavior. For the class data, you only need to plot 7-10 points to get the general shape of the titration curve. In your lab notebook (or using Excel), you should make a much more detailed plot.

14. Record the class data for every acid studied. You will need the concentration, the initial pH, the pH at $\frac{1}{2} V_{eq}$, pH at $V_{eq}$, and the final pH. An example table is provided in the description of the lab report.
Using a Titration Curve to Calculate the Equivalence Point

From the graph of your titration, extrapolate straight lines similar to lines BF, GE, and JI. The equivalence point will be the midpoint in line JI, which you can measure with a ruler. Mark the equivalence point with an X, then draw a line straight down to the x-axis. This marks the volume at equivalence, or $V_{\text{eq}}$. The volume at $\frac{1}{2}$ equivalence is equal to $V_{\text{eq}} \div 2$. The pH at $\frac{1}{2}$ equivalence is equal to the pKa for the weak acid. Why is pH = pka at $\frac{1}{2}$ equivalence?

A five gallon bucket will be provided for disposal of all the waste solutions from this experiment.
### Table 1. Titration data for various solutions.

<table>
<thead>
<tr>
<th></th>
<th>initial pH</th>
<th>pH at ½ equivalence</th>
<th>Volume at equivalence</th>
<th>final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010 M HNO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.020 M HNO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.030 M HNO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005 M H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.010 M H₂SO₄</td>
<td></td>
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</tr>
<tr>
<td>0.020 M H₂SO₄</td>
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<tr>
<td>0.005 M H₂SO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0.010 M H₂SO₃</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0.020 M H₂SO₃</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.005 M NaCO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.010 M NaCO₃</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.020 M NaCO₃</td>
<td></td>
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</tr>
</tbody>
</table>

### Results and Discussion:

1) Which of the acids studied are weak? Which are strong? How can you tell from the data?

2) Calculate the pKa for the weak acid from the Ka values given in the lab manual. How does the experimentally determined pKa compare with the calculated values?

3) Choose two diprotic acids of the same concentration, what is the volume at equivalence for each? Comment on the similarities.
Generate a good graph of pH vs. Volume Titrant for your sample and attach it to this report. Use a graphing program like Excel.

4) The A buffer resists changes to pH. For the solution you titrated, identify the buffer region on the graph.

Acid Rain and Buffers

In the Midwest, the natural geologic formations are typically made of limestone (CaCO\(_3\)). The limestone in the Midwest provides the lakes and soils with a natural buffer.

**Pure Water**

5) What is the pH of 1.000L of pure water?

6) A 200.00 mL sample of 1.000M nitric acid was added to the water sample above. What is the resulting pH?

**Carbonate Buffer**

7) What is the pH of a carbonate buffer solution prepared by mixing 1.500 mol Na\(_2\)CO\(_3\) and 1.000 mol of NaHCO\(_3\) and adding water to make a 1.000L solution? (pKa of HCO\(_3\)\(^-\) is 10.32)

8) A 200.00 mL sample of 1.000M nitric acid was added to the buffered solution above. What is the resulting pH?

9) Explain conceptually the process by which the limestone can protect the lakes in the Midwest.