Experiment 3

Gravimetric Analysis of a Sulfate Mixture

Experimental Objectives

- To determine the relative percentages of sodium and potassium sulfates in an unknown mixture.
- To determine the mass percent of sulfate in a solid unknown. (Inquiry)

AP Learning Objective

1.19: The student can design, and/or interpret data from, an experiment that uses gravimetric analysis to determine the concentration of an analyte in a solution.

AP Science Practices

4.2: The student can *design a plan* for collecting data to answer a particular scientific question.

5.1: The student can *analyze data* to identify patterns or relationships.

Concepts

Gravimetric analysis, stoichiometry, mole ratios

Introduction

In this experiment you will be given a sample that contains sulfate ions. It is a mixture of two compounds, sodium sulfate and potassium sulfate, both anhydrous salts. Your first task is to determine the total number of moles of sulfate ion in the original mixture. From that quantity and using the total mass of your sample and the molar masses of the two components of the mixture, you will be able to determine the composition of the sulfate mixture.

This requires careful technique. Your results will be evaluated in part on how close you come to the actual composition of the mixture. The sulfate mixture will dissolve in water. When an aqueous solution of barium chloride is added to the solution, insoluble barium sulfate will precipitate from the solution.

$$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s) \qquad \textit{(Equation 3–1)}$$

The precipitate is collected by centrifugation, washed carefully, dried and weighed. This experiment is an example of *gravimetric analysis*. You can expect to spend about an hour on the first day, plus short periods of time on one or more successive days, perhaps while another experiment is in progress.

Prelaboratory Assignment

1. Read the entire experiment before coming to the laboratory.
2. Prepare a data table for recording masses and descriptive observations.

Prelaboratory Questions

1. Write the balanced molecular and complete-ionic equation for the reaction between barium chloride and potassium sulfate in aqueous solution to form barium sulfate. Show that the net-ionic equation for this reaction is the same as was given above.
2. Suggest a reason why it is desirable to use an excess of barium ion in the precipitation.

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3. A sample of an unknown sulfate compound has a mass of 0.1000g. Addition of excess barium chloride solution to the sample forms a barium sulfate precipitate of mass 0.0676g. What is the mass percent of sulfate ion in the unknown compound?
4. Hydrated calcium sulfate, $CaSO_4 \cdot H_2O$, contains 55.8% sulfate ion by mass. Calculate the number of waters of hydration present in the hydrate. Write the correct formula for the hydrate.

Safety Precautions

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. Hydrochloric acid is corrosive to skin and clothing.
3. Barium compounds are toxic. Wash your hands thoroughly with soap and water before leaving the laboratory.

Materials

Apparatus

milligram balance

100-mm test tube

small hotplate

Desiccator

Centrifuge

Reagents

solid mixture of potassium sulfate, K_2SO_4 and sodium sulfate, Na_2SO_4

1.0 *M* HCl

1.0 *M* $BaCl_2$

Sulfate unknown; a sample of an unknown sulfate salt

Procedure – Skills

For the most precise results, duplicate determinations should be carried out, each according to the procedure described below. The sample mass should be in the range of 100-150 mg if a balance with milligram sensitivity is used, or 50-100 mg if an analytical balance is available.

Note: If your sample has an identifying number or letter, be sure to record the identifier in your notebook.

1. Determine the mass of a clean, dry 100-mm test tube. Place a small amount of the unknown (about the volume equivalent of one grain of rice) in the tube, then reweigh the tube and contents. Add about 1 mL of distilled water to dissolve the sample, gently warming the tube on a hot plate or *carefully* in a burner flame if necessary. Some solids may require more water, but be careful not to fill the tube beyond about $^1/_3$ full. The sample must be completely dissolved before proceeding.
2. Add 2 drops of 1 *M* HCl to the tube and shake gently. Follow this with 0.5-1.0 mL of 1.0 *M* $BaCl_2$ added dropwise, with gentle shaking after each 2-3 drops. Take care not to get barium chloride on your skin; if you do, wash it off with soap and water. Warm the tube and contents on a hotplate or in a hot-water bath for 2-3 minutes to aid coagulation of the precipitate. Do not boil.
3. Remove the tube from the heat (dry the outside, if necessary), allow it to cool, then centrifuge for 30 seconds. Your teacher will provide instruction on using the centrifuge. Without disturbing the solid on the bottom of the test tube, add one more drop of the barium chloride solution. If no new cloudiness appears in the liquid, proceed with the washing of the precipitate (step 4). If cloudiness is observed, add five more drops of the $BaCl_2$, then heat, centrifuge, and test again with barium chloride; continue in this fashion until addition of barium chloride does not cause further cloudiness.
4. Decant and discard the clear supernatant solution above the barium sulfate precipitate, being careful not to lose any solid. A microtip transfer pipet or Pasteur pipet is useful for this purpose. Add about ten drops of ice-cold distilled water to the solid in the tube, then shake the tube and contents until all

cloudiness appears in the liquid, proceed with the washing of the precipitate (step 4). If cloudiness is

of the precipitate is suspended in the water (it will not dissolve). Centrifuge the suspension and again discard the clear, colorless supernatant, being careful not to lose any of the white solid. Repeat the ice-water rinse, centrifuging, and decanting twice more, followed by a final rinsing with acetone.

5. Dry the test tube and precipitate, first on a steam bath[1] to drive off most of the acetone and then in a 105-110°C oven for at least one hour, preferably overnight.

6. Remove the tube from the oven and allow it to cool for a minimum of 30 minutes in a desiccator. Determine the mass of the tube and contents. Return the tube to the oven for at least an hour, cool in the desiccator once more, then reweigh it. If the mass agrees within experimental error (± 0.5% of the precipitate mass) with the previous value, the experiment is completed. If not, continue the cycle of oven-drying, cooling, and weighing until a constant mass is obtained.

Disposal

1. Barium sulfate, like barium chloride, is toxic by ingestion. Transfer your solid product to an appropriate container for removal as hazardous waste. Small amounts of barium ion were washed into the effluent stream during the decanting and rinsing portions of the procedure; this is unavoidable, but the amounts are below the parts-per-trillion level, so are not a significant hazard to the environment.

2. Wash all glassware immediately after use and return it to its proper location.

Processing the Data

Determine each of the following, showing appropriate calculations to support your results. If you did two or more trials, as was suggested, you need only show calculations for one of the trials, with results for all presented in the form of a table, with separate columns for each sample.

- Mass of original sulfate sample
- Mass and moles of barium sulfate produced
- Moles and mass of sulfate ion present in unknown sample
- Mass percent of sulfate ion in unknown

The unknown that you used was a mixture of potassium sulfate, K_2SO_4, and sodium sulfate, Na_2SO_4. Here's what you know:

- The total number of moles of sulfate must equal the combined moles of K_2SO_4 and Na_2SO_4.
- The total mass of the original sample must be the combined masses of K_2SO_4 and Na_2SO_4.
- The number of moles of K_2SO_4 is found by dividing the mass of K_2SO_4 by the molar mass of K_2SO_4; likewise, the moles of Na_2SO_4 is found by dividing the mass of Na_2SO_4 by the molar mass of Na_2SO_4.
- The mass of K_2SO_4 must be the difference between the total mass of the original sample and the mass of Na_2SO_4 in that sample.

Given this information it is a simple matter of algebra to determine the masses of K_2SO_4 and Na_2SO_4 that were in the original sample, and from those you can establish the mass percent composition of the sample mixture. Thus, for an original sample mass of 0.125 g, if the mass of K_2SO_4 is represented by x, the mass of Na_2SO_4 would be $0.125 - x$. If you carried out multiple trials, you need only show the actual calculations for one trial; simply report the masses of K_2SO_4 and Na_2SO_4, and the percentage composition of the mixture for any additional trials.

[1] A hotplate on very low setting will also work reasonably well. Stand the tube in a small beaker to prevent roll-off and to allow steam to escape.

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5.1: The student can *analyze data* to identify patterns or relationships.

Concepts

Gravimetric analysis, stoichiometry, mole ratios

Introduction

In this experiment you will be given a sample that contains sulfate ions. It is a mixture of two compounds, sodium sulfate and potassium sulfate, both anhydrous salts. Your first task is to determine the total number of moles of sulfate ion in the original mixture. From that quantity and using the total mass of your sample and the molar masses of the two components of the mixture, you will be able to determine the composition of the sulfate mixture.

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3. Barium compounds are toxic. Wash your hands thoroughly with soap and water before leaving the laboratory.

Materials

Apparatus	*Reagents*
milligram balance	solid mixture of potassium sulfate, K_2SO_4 and sodium sulfate, Na_2SO_4
100-mm test tube	1.0 *M* HCl
small hotplate	1.0 *M* $BaCl_2$
Desiccator	Sulfate unknown; a sample of an unknown sulfate salt
Centrifuge	

Procedure – Skills

For the most precise results, duplicate determinations should be carried out, each according to the procedure described below. The sample mass should be in the range of 100-150 mg if a balance with milligram sensitivity is used, or 50-100 mg if an analytical balance is available.

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3. Remove the tube from the heat (dry the outside, if necessary), allow it to cool, then centrifuge for 30 seconds. Your teacher will provide instruction on using the centrifuge. Without disturbing the solid on the bottom of the test tube, add one more drop of the barium chloride solution. If no new cloudiness appears in the liquid, proceed with the washing of the precipitate (step 4). If cloudiness is observed, add five more drops of the $BaCl_2$, then heat, centrifuge, and test again with barium chloride; continue in this fashion until addition of barium chloride does not cause further cloudiness.
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5. Dry the test tube and precipitate, first on a steam bath[1] to drive off most of the acetone and then in a 105-110°C oven for at least one hour, preferably overnight.

6. Remove the tube from the oven and allow it to cool for a minimum of 30 minutes in a desiccator. Determine the mass of the tube and contents. Return the tube to the oven for at least an hour, cool in the desiccator once more, then reweigh it. If the mass agrees within experimental error (± 0.5% of the precipitate mass) with the previous value, the experiment is completed. If not, continue the cycle of oven-drying, cooling, and weighing until a constant mass is obtained.

Disposal

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Processing the Data

Determine each of the following, showing appropriate calculations to support your results. If you did two or more trials, as was suggested, you need only show calculations for one of the trials, with results for all presented in the form of a table, with separate columns for each sample.

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The unknown that you used was a mixture of potassium sulfate, K_2SO_4, and sodium sulfate, Na_2SO_4. Here's what you know:

- The total number of moles of sulfate must equal the combined moles of K_2SO_4 and Na_2SO_4.
- The total mass of the original sample must be the combined masses of K_2SO_4 and Na_2SO_4.
- The number of moles of K_2SO_4 is found by dividing the mass of K_2SO_4 by the molar mass of K_2SO_4; likewise, the moles of Na_2SO_4 is found by dividing the mass of Na_2SO_4 by the molar mass of Na_2SO_4.
- The mass of K_2SO_4 must be the difference between the total mass of the original sample and the mass of Na_2SO_4 in that sample.

Given this information it is a simple matter of algebra to determine the masses of K_2SO_4 and Na_2SO_4 that were in the original sample, and from those you can establish the mass percent composition of the sample mixture. Thus, for an original sample mass of 0.125 g, if the mass of K_2SO_4 is represented by x, the mass of Na_2SO_4 would be $0.125 - x$. If you carried out multiple trials, you need only show the actual calculations for one trial; simply report the masses of K_2SO_4 and Na_2SO_4, and the percentage composition of the mixture for any additional trials.

[1] A hotplate on very low setting will also work reasonably well. Stand the tube in a small beaker to prevent roll-off and to allow steam to escape.

Analysis and Conclusions

1. Suggest explanations for each of the following parts of the procedure.
   a. The first three rinsings of the product specified the use of distilled water that was ice-cold, rather than at room temperature.
   b. Acetone is used for the final rinse.
2. What would be the effect on your determination of the mass of barium sulfate in each of the following cases? For each one, you are to decide whether the reported percentage of sulfate would be too high, too low, or unaffected. Explain the reasoning behind your choice.
   a. Too little barium chloride solution was used.
   b. The sample was not thoroughly dried.
   c. The tube and contents were not cool before the final weighing.
3. The purpose of adding hydrochloric acid in Part B is to remove any carbonate ions that might be present in the unknown, so that barium carbonate will not precipitate along with the sulfate. Write the net-ionic equation for the reaction between protons (hydrogen ions) in solution and dissolved carbonate ions.
4. What effect on your sulfate percentage could result if the addition of acid were omitted? Explain.
5. **Error Analysis:** Discuss experimental errors and identify those portions of the procedure where extra care is needed to ensure satisfactory results. If multiple trials were conducted, determine the percent deviation between or among those trials.

Inquiry

The Challenge. Your teacher will give you a sample of an impure sulfate compound. You will be told what the cation is. You are to determine the percent purity of the sulfate-containing compound. By determining the mass percent of sulfate ion in the impure salt you should be able to determine the percent purity. You will be given enough of the salt to do at least three determinations. The same materials will be available, including 1.0 *M* HCl(aq) and 1.0 *M* $BaCl_2$(aq).

Assignment. You and your partner are to submit to your teacher a detailed procedure, describing the exact sequence of steps you expect to follow, the data to be collected, and any calculations that will be carried out. Be sure to reference your answer to Analysis and Conclusions question #5 as you develop your strategy for accomplishing your goal. You are to include sections on Safety and Cleaning Up as part of your plan. Assume that the anhydrous solids remaining at the end of your experiment will be collected for later disposal or re-use.

Once your teacher has determined that your plan is complete and safe, you will be allowed to conduct your experiment. Note that teacher approval is not a guarantee that your plan will be successful.

Following completion of your experimental procedure, carry out the appropriate calculations to determine the mass percent of sulfate ion in your unknown.

Experiment 11

Rate Law Determination

Experimental Objectives

To determine the rate law and the specific rate constant for a chemical reaction

AP Learning Objectives

4.2: The student is able to analyze concentration vs. time data to determine the rate law for a zeroth-, first-, or second-order reaction.

AP Science Practices

5.1: The student can *analyze data* to identify patterns or relationships. (*Connects to Essential knowledge 4.A.3*: The magnitude and temperature dependence of the rate of reaction is contained quantitatively in the rate constant.

Concepts

Reaction kinetics, reaction order, reaction mechanisms, effect of temperature on reaction rates

Introduction

As you know from Experiment 4, *Analysis of Vinegar*, the acid-base indicator phenolphthalein is colorless in acidic or neutral solutions and turns bright magenta as the solution becomes basic. In strongly basic solutions the red color slowly fades and the solution again becomes colorless. The kinetics of this "fading" reaction can be traced spectrophotometrically. Graphical treatment of the results allows us to determine the order of reaction.

Phenolphthalein is a large organic molecule. In solutions where the pH < 8, it has the structure shown in **Figure 11.1**, which is colorless. As [OH^-] increases and the solution becomes alkaline (basic), the phenolphthalein molecule (abbreviated $\mathbf{H_2Ph}$) loses two hydrogen ions to form the magenta dianion (abbreviated $\mathbf{Ph^{2-}}$), as shown in **Figure 11.2**.

The colorless-to-red transition of H_2P to P^{2-} (*Equation 11-1*) is very rapid and the red color develops instantly when the pH reaches the indicated range. Gradually, however, if the concentration of hydroxide ions remains high, the red P^{2-} dianion will combine with hydroxide ions to form a third species, $\mathbf{PhOH^{3-}}$ (**Figure 11.3**; *Equation 11-2*), which is also colorless. The rate of this second reaction is much slower than the first and depends on the concentrations of phenolphthalein and hydroxide ions.

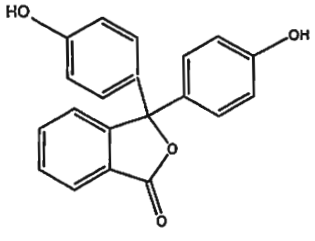

Figure 11.1: H_2Ph

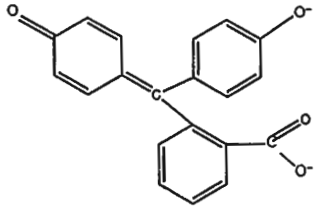

Figure 11.2: Ph^{2-}

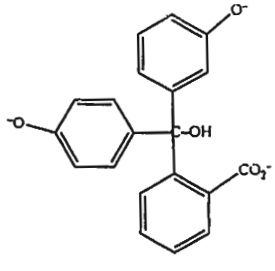

Figure 11.3: $PhOH^{3-}$

$$2OH^-(aq) + H_2Ph(aq) \rightarrow Ph^{2-}(aq) + 2H_2O(\ell) \qquad \textit{(Equation 11-1)}$$

Colorless *Red*

Followed by

$$Ph^{2-}(aq) + OH^-(aq) \rightarrow PhOH^{3-}(aq) \qquad \textit{(Equation 11-2)}$$

Red *Colorless*

Figure 11.1: H_2Ph Figure 11.2: Ph^{2-} Figure 11.3: $PhOH^{3-}$

The kinetics of the reaction can be followed by tracing the color intensity due to Ph^{2-} as a function of time and graphing the results. Figure 11.4 illustrates how the concentration of a reactant decreases with time over the course of a reaction. Notice that the graph of concentration versus time is not a straight line, but rather curves downward, leveling over time, showing that the reaction slows down as the reactant concentration decreases.

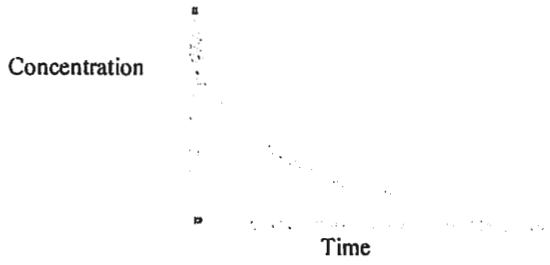

Figure 11.4 Typical Plot of Concentration vs Time

Exactly how much the rate decreases as the reactant concentration decreases depends on the rate law for the reaction. In the case of the reaction of Ph^{2-} with OH^- ions, the *rate law* has the general form

$$\text{Rate} = k[Ph^{2-}]^m[OH^-]^n \qquad \textit{(Equation 11-3)}$$

The exponents, m and n, are defined as the *order of reaction* with respect to the concentration of each reactant, and k is the specific rate constant for the reaction at a particular temperature. The values of the exponents m and n must be determined by experiment. If the reaction is carried out under conditions where the concentration of OH^- does not change, which may be accomplished by using a large excess of hydroxide ions, then the rate law will reduce to the form:

$$\text{Rate} = k'[Ph^{2-}]^m \qquad \textit{(Equation 11-4)}$$

where k' is a "pseudo" rate constant, incorporating both the overall rate constant k and the $[OH^-]^n$ term: $k' = k_{overall}[OH^-]^n$. This is valid so long as the value of $[OH^-]$ is constant, within experimental uncertainty.

Mathematical treatment of the equations for the reaction rate and the rate law predicts the following outcomes:

- If the fading reaction is zero order in $[Ph^{2-}]$ (if $m = 0$), the plot of $[Ph^{2-}]$ versus time will be linear.
- If the fading reaction is first order in $[Ph^{2-}]$ (if $m = 1$), a graph of the natural log (ln) of $[Ph^{2-}]$ versus time will give a straight line with a slope $= -k'$.
- If the fading reaction is second order in $[Ph^{2-}]$ (if $m = 2$), a graph of $1/[Ph^{2-}]$ versus time will give a straight line with a slope $= +k'$.

Experiment Overview

The stated goal of this experiment is to use *colorimetry* and graphical analysis to determine how the rate of a dye-fading reaction depends on the concentration of the dye. A colorimeter is a special instrument that measures the absorbance of light. A known amount of dye will be added to a large excess of sodium hydroxide. The instrument measures the percentage of light of a particular wavelength that passes through the solution, then converts the percent transmittance (%T) to a property known as the *absorbance (Abs)*. This absorbance of the solution will be measured at specific time intervals.

A relationship known as the Beer-Lambert Law, takes the form:

$$\text{Abs} = \varepsilon \cdot l \cdot c \qquad \textit{(Equation 11-5)}$$

where ε, *the molar absorptivity*, is a function of the colored species involved (the "absorbing" species), l *is the length of the path the light travels* through the solution (the width of the cuvette), and c *is the concentration of the absorbing species*, in $\text{mol} \cdot \text{L}^{-1}$. For a series of measurements involving the same species in the same holder (such as a cuvette), ε and l are constant, so $(\text{Abs}/c) = \varepsilon \cdot l$ = a constant, and a plot of absorbance vs. concentration must be linear. You have previously made plots of absorbance vs.

This absorbance of the solution will be measured at specific time intervals.

concentration, and so have verified this linearity for yourself.[1] Such plots are called Beer's Law plots. For an extended discussion, see the section titled *Spectral Analysis* in the Appendix section of your text.

In this experiment, Beer-Lambert Law is not useful here, since the colorimeter is reading continuously as the concentration of the absorbing species decreases. Because the concentration change is due to a chemical change taking place, and since the rate of a reaction diminishes over time, your plot will be curved, rather than linear, as shown earlier in Figure 11.4.

Even so, absorbance is directly proportional to concentration, so a graph of absorbance versus time has the same characteristics as a graph of concentration versus time as in Figure 11.4. Graphing functions of the absorbance data (ln *Abs* versus time, and 1/*Abs* versus time) should reveal whether the fading reaction is first or second order in the dye.

Prelaboratory Assignment

1. Read the entire experiment before coming to the laboratory.
2. Review the concept of differential rate laws for 0^{th}, 1^{st}, and 2^{nd} order reactions, including the use of graphical techniques to determine the value of the specific rate constant
3. Be sure you are familiar with the operation of the colorimeter you are to use for tracing the progress of the reactions.

Prelaboratory Questions

1. Consider the following data for a series of readings in a hypothetical experiment similar to the ones you will be doing. Copy the table into your notebook, then complete the table as described below and on the following page. These data were obtained using a different dye substance, malachite green.

Time	Abs	ln(Abs)	$(Abs)^{-1}$
0	0.7546		
1	0.7344		
2	0.6966		
3	0.6619		
4	0.6323		
5	0.6021		
6	0.5694		
7	0.5390		
8	0.5126		
9	0.4858		
10	0.4605		

   a. Calculate the values of ln(Abs) and 1/Abs for each absorbance measurement to complete the table. To do this, clear Lists L1, L2, L3, and L4 of your graphing calculator, then enter the numbers of minutes (1, 2, ..., 10) in L1, and the absorbance values in L2. Now follow the direction for Analyzing the Results, starting with the second paragraph. Enter the values you obtain for ln(Abs) and 1/(Abs) in the appropriate columns of the table in your notebook.
   b. Using your calculator, view plots of ln(Abs) versus time and 1/Abs versus time. Your teacher may require you to plot by hand, using graph paper or the quadrille pages of your laboratory notebook. If so, each graph should occupy about ½ page.
   c. Using the Curve Fit option, determine the correlation coefficient ("R") value for each plot. Which graph more closely approximates a straight line? Is the reaction first or second order?
   d. What is the value of the specific rate constant, *k*, for this reaction? (Note: this is actually a pseudo-rate constant.)
2. Explain why, as the Experiment Overview asserts, "Absorbance is directly proportional to" the concentration of the colored species in solution.

[1] Experiments 1 and 2 of this manual.

graph more closely approximates a straight line? Is the reaction first or second order?

3. In this experiment, the species you will be investigating is red in color. Why do we not set the colorimeter to the setting for red, rather than green light?
4. The discussion on page 3, above, asserts that the slope of whichever plot is linear will have a magnitude equal to the value of the specific rate constant *k*. Use the integrated form of the first and second order rate laws to show that this is the case. How can graphical treatment of absorbance data be used to determine the value of *k* for a 1st order reaction? for a 2nd order reaction?
5. Each of the three runs you will do in the Skills portion of the experiment uses 3.0 mL of 5.0×10^{-4} *M* Ph and 0.25 mL of 0.20 *M* NaOH.
   a. Calculate the initial concentrations of Ph and OH^- at the instant of mixing, before reaction has begun.
   b. Calculate the concentration of OH^- in the solution once all of the Ph has reacted. Assume that OH^- and Ph react 1:1.
   c. Based on your calculations, is it correct to state, as you read in the Introduction, that the molar concentration of hydroxide ion remains constant throughout the experiment, within experimental uncertainty? Give evidence to support your answer.

Materials

Apparatus

Cuvette with lid (at least 1, up to 3)

Colorimeter sensor or spectrophotometer with recording capability

Computer interface system (LabPro or similar)

Computer or calculator for data collection

Data collection software (e.g., LoggerPro™)

Tissues or lens paper, lint-free

Pipets for measuring solutions – See note 3, below.

Reagents

Phenolphthalein (Ph) solution, 5.0×10^{-4} *M*

Sodium hydroxide, NaOH, 0.20 *M*

Wash bottle and distilled water

Safety Precautions

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. Sodium hydroxide is a corrosive liquid. Avoid contact with eyes and skin and clean up all spills immediately.
3. Phenolphthalein is moderately toxic by ingestion and has distinct laxative properties. Wear chemical splash goggles and chemical-resistant gloves and apron.
4. Wash hands thoroughly with soap and water before leaving the laboratory.

Notes

1. **Cuvettes** – Handle the cuvette by its ribbed sides or its top to avoid getting fingerprints on the optical surface. The plastic cuvettes typically used in Vernier colorimeters have a capacity of about 3.5 mL. A single cuvette lid can be used for all three trials, but 3 separate cuvettes, one for each trial, saves a good deal of time.

   Always wipe the cuvette with a lint-free tissue (e.g. KimWipe™) before placing it in the colorimeter. Never place a wet cuvette in the colorimeter.

   The reference mark on the cuvette should always face toward the white reference mark on the cuvette slot of the colorimeter. (For plastic cuvettes, simply make sure that the ribbed sides are at right angles to the light path.
2. Connect the interface system to the computer or calculator and plug the colorimeter sensor into the interface.

3. Plastic transfer pipets, with stems calibrated in 0.25-mL intervals, are sufficiently precise for purposes of this part of the experiment.
4. In principle, the colorimeter will heat up over time, but the runs here are of such short duration that the slight increase in temperature should make no difference.

Procedure – Skills

1. Given the wide variety of electronic devices using colorimeters, no one set of instructions will do for all. Be sure you understand the operation of the interface you will be using. Set it to take readings at least once each three seconds (1/second is ok), for a period of 600 seconds (10 minutes). Set the wavelength at 565 nm.
2. For calibration purposes, prepare a "blank" cuvette containing 3.0 mL of 0.20 *M* NaOH. Place the cap on the cuvette. With the blank in the sample chamber, calibrate the colorimeter at 565 nm, as directed in the instructions that accompany the colorimeter.
3. This step is to be carried out three separate times. Each trial is to be followed by the process described below in **Analysis and Conclusions.**

   Remove the cuvette containing the 3.0 mL of 0.20 *M* NaOH from the sample chamber. Remove the cap from the cuvette, then *working quickly but carefully*, add 0.25 mL of 5.0×10^{-4} *M* Ph to the same cuvette; this will result in a dark magenta color. Immediately place the lid on the cuvette and carefully invert the cuvette a couple of times to mix the solution, wipe the smooth faces of the cuvette with a lint-free tissue and place the cuvette in the colorimeter compartment. Note the absorbance reading being displayed; it may show an increase in absorbance at first.

   As soon as the absorbance starts decreasing start the run to begin measuring time. This ensures that the absorbance versus time measurements will accurately reflect the time of reaction from the time of mixing.
4. Allow the interface to continue making absorbance measurements until the end of the run. When 10 minutes has elapsed, the system will discontinue readings. For most instruments, once the run is complete it will re-draw the graph of absorbance vs. time, with the Absorbance scale adjusted to give a full-screen plot. Remove the cuvette from the colorimeter compartment.
5. If possible, save the data on the computer or calculator and use a program such as Graphical Analysis to obtain a printout of the absorbance versus time data table and graph. Otherwise, you will need to record the absorbance and time measurements in a data table. (In EasyData, the data will be found in lists L1 and L2.)[2] Newer, stand-alone interfaces allow you to do the manipulations right on the instrument.
6. Proceed to **Analysis and Conclusions**. Complete that section for the first run and record the Correlation value, or "R" (for regression) values for the curve fitting of ln(Abs) vs. time and for $(Abs)^{-1}$ vs time, if available. If your interface cannot provide that information, you can use a spreadsheet program to accomplish the same goal.

[2] For older calculators, you can accomplish the same thing using the DataMate application, which can be loaded directly from a CBL2 or LabPro interface.

Analyzing The Results

(Note: What follows applies to users of calculator-based interfaces, CBL2 and LabPro. For other systems, consult your teacher for how to carry out the analysis. After viewing the re-drawn graph, answer Analysis and Conclusions question 1, then press ENTER. This will return you to the main menu. Select option 6, QUIT.[3] The screen will tell you that time is in L1 and CH1 is in L2; press ENTER.

On your calculator, select STAT, then EDIT. This will display the lists of time (L1) and absorbance (L2). Scroll up to the top ("banner") of L1, then across to L3. Press ENTER. Select LN. The screen will show, "LN(." Press 2nd L2 (L2 is the 2nd function of the "2" key). The calculator will fill L3 with the natural log (ln) of each value in L2, thus these are the values of ln (Abs).

Now scroll to the banner of L4. This time, select L2, followed by the x^{-1} key. L4 now contains the corresponding values for 1/(Abs). You will use these in the Analysis and Conclusions section, below.

Printing the Graphs

In this Skills portion of the experiment you are concerned only with which plot is most nearly linear, you can view the graphs directly on your calculator screen by setting up the various plot options (2nd, STAT PLOT) to plot L1 on the x axis and L2, L3, L4 on the y-axis of Plot 1, Plot 2, and Plot 3, respectively. Options include Graph-Link™ (but the process is a tedious one), and use of a USB or Graph-Link™ cable, and the Vernier program, Graphical Analysis™ to transfer the lists to a computer for printing. Open Graphical Analysis and follow the directions for transferring lists ("Transfer From TI"). For those who are using LabQuest, Vernier has recently released an app for iPad that you may find helpful.

Analysis and Conclusions – Skills

Note: The discussion that follows is specific to the EasyData and DataMate applications (Vernier Scientific), used with LabPro and CBL2 calculator-based interfaces. Stand-alone interfaces (e.g. LabQuest) will accomplish the same goals, without having to exit the application software. Consult your teacher or the documentation supplied by the manufacturer.

1. Examine the shape of the graph of absorbance vs. time. Is it linear or curved? What does that tell you about the order of the reaction with respect to phenolphthalein concentration?
2. If you are using an instrument that allows you to plot the various functions of absorbance on a screen, there is no need to record the values yourself. (This would apply to CBL2, LabPro, and LabQuest, for example.) Otherwise, you will need to prepare a table in your notebook using the same headings found in Prelaboratory Question 1, but that's a laborious and time-consuming process. Enter the values of time, absorbance (Abs), ln(Abs), and 1/Abs for each set of readings made by the colorimeter.
3. Plot or obtain graphs (on the interface screen, if possible) of both ln(Abs) versus time and of $[Abs]^{-1}$ versus time. Hand-drawn plots should be drawn with care, and properly labeled. Draw the best smooth fit through the points. If the graph appears to be a straight line, use a ruler or straightedge to make the best-fit line. If the line appears to be curved, draw the best-fit smooth curve through the points.
4. Which graph more closely approximates a straight line? Is the reaction of Ph with hydroxide ions first or second order in [Ph]? You can answer that question quickly and easily, using the DataMate column and the values you have put in L3 and L4. Here's how.

   Return to the EasyData application. If you have disconnected your calculator from the interface, select NO INTERFACE, when prompted. This will take you to the Main Menu screen. Select ANALYZE, followed by CURVE FIT, on the ANALYZE OPTIONS screen.

[3] Don't panic! Your data will remain stored on your calculator until you overwrite it. You can always return to DataMate and view your graph.

The application (DataMate or EasyData) "thinks" that L3 contains data collected from Channel 2, and that L4 contains data from Channel 3. Select LINEAR (CH2 VS TIME). Since L3 (CH2) contains the values of ln (Abs), this will give you a plot of ln (Abs) vs time. The first screen you will see contains the A and B values for the curve in the form Y = AX + B; the R value (the correlation coefficient) is a measure of how linear the graph will be. The closer it is to 1.000000, the more linear the graph. Values of R larger than 0.999 represent good linearity, while a value of 0.98 or less means that the plot will more likely be a curve. Note and record the value of R, then press ENTER to look at the plot and to see the calculator draw a best-fit straight line through the points.

Work your way back to the ANALYZE OPTIONS menu. Choose CURVE FIT again, but this time select LINEAR (CH3 VS TIME), to get information about the plot of 1/Abs vs. time. Again the R-value is the test of linearity.

Note. Remember that you're working with the first part of the curve of concentration vs. time, so all three plots, including Abs vs. time are going to be fairly linear. The R-value is your best key to deciding what the order of reaction is. As an example, in a recent test of the experiment, the lowest value of R was –(0).986788413 (the minus sign indicates a negative slope), while the other two were (0).9969259604, and –(0).9990384299, respectively. (These are in order from lowest to highest, not necessarily CH1, CH2, and CH3. It is common for the highest R-value to round to 0.9999.)

5. Determine the value of k', the pseudo-specific rate constant for the reaction. Be sure to include its units. For time, use seconds, rather than minutes.

6. The rate constant you determined above is actually a pseudo rate constant, k', and is equal to the actual rate constant, k, multiplied by the concentration of hydroxide ion, raised to a power that represents the order of reaction with respect to hydroxide ion concentration. Thus, $k' = k[OH^-]^m$, where m is the order with respect to hydroxide ion concentration.

   a. Assume $m = 1$; determine the value of k, including units.
   b. Assume $m = 2$; determine the value of k, including units.

Inquiry

You and your partner are to design and, with your teacher's approval, execute a plan to determine both the order of reaction with respect to hydroxide and the overall rate constant for the reaction between phenolphthalein and sodium hydroxide. In the terms of *Equation 11-3* of the Introduction, you're seeking values for n and k.

Topic for Additional Investigation

As was noted under Analysis and Conclusions, you're working with the first part of the concentration vs. time curve for the dye-fading reaction. Working with your partner, see if you can come up with a way to adapt this experimental procedure to use the method of initial rates to determine the overall rate law for the phenolphthalein – hydroxide color fading system.

Experiment 10

Investigating Reaction Rates

Experimental Objectives

To determine the rate law and the specific rate constant for a chemical reaction

AP Learning Objectives

4.1: The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the rate of a reaction.

AP Science Practices

4.2: The student can *design a plan* for collecting data to answer a particular scientific question.

5.1: The student can *analyze data* to identify patterns or relationships.

Concepts

Reaction kinetics, reaction order, reaction mechanisms, effect of temperature on reaction rates

Introduction

One of the goals of chemical kinetics is to determine, as best we can, the sequence of steps that take place in chemical reactions. This sequence of steps is called the *reaction mechanism*. According to collision theory, any single step is unlikely to involve more than two molecules since the possibility of more than two molecules meeting at the same instant and all molecules having the proper spatial orientation is statistically improbable. When a reaction proceeds via a sequence of steps, the rate of the reaction is governed by the slowest of the steps, called the *rate determining step*.

The particular reaction which you will be investigating is the one that occurs between iodate ions, IO_3^-, and hydrogen sulfite ions, HSO_3^-, commonly called bisulfite ions. The balanced equation for the overall reaction is:

$$5\ HSO_3^-(aq) + 2\ IO_3^-(aq) \rightarrow I_2(aq) + 5\ SO_4^{2-}(aq) + H_2O(l) + 3\ H^+(aq) \qquad (Equation\ 10\text{-}1)$$

But what you will see is actually a multi-step process, as follows:

$$(1)\ 3\ HSO_3^-(aq) + IO_3^-(aq) \rightarrow I^-(aq) + 3\ SO_4^{2-}(aq) + 3\ H^+(aq)\ (slow)$$

$$(2)\ 6\ H^+(aq) + 5\ I^-(aq) + IO_3^-(aq) \rightarrow 3\ I_2(aq) + 3\ H_2O(l)\ (fast)$$

The molecular iodine in solution will form a dark blue complex with the starch that's present, but so long as any bisulfite ion remains, side-reaction (3) will take place, converting $I_2(aq)$ to $I^-(aq)$, before the complex can form.

$$(3)\ I_2(aq) + HSO_3^-(aq) + H_2O(l) \rightarrow 2\ I^-(aq) + SO_4^{2-}(aq) + 3\ H^+(aq)$$

As soon as the bisulfite is used up, the reaction in (2) takes place, and the mixture flashes to dark blue.

Your first task in this experiment is to determine the order of reaction with respect to iodate concentration, which we will represent as $[IO_3^-]$. You will be guided through the process and the calculations for doing so. Then, if your teacher directs you to do so, you may be asked to devise a plan to determine the order with respect to bisulfite ion concentration, represented by $[HSO_3^-]$.

The rate law for the reaction takes the form

$$rate = k[IO_3^-]^m[HSO_3^-]^n \qquad (Equation\ 10\text{-}2)$$

You will also investigate the effect of changing temperature on this reaction system. As you know, the Arrhenius equation enables the use of such data to determine the activation energy, E_a, for a reaction.

with respect to bisulfite ion concentration, represented by $[HSO_3^-]$.

Here's what you know about the reaction. Iodate is a strong oxidizing agent: it can oxidize bisulfite to sulfate, as shown in *Equation 10-1*. But bisulfite can act as a reducing agent on the products of that reaction, rapidly converting molecular iodine to iodide ions.

By design, the concentration of bisulfite ion is kept lower than that of the iodate, so once all the bisulfite has been consumed, any remaining molecular iodine reacts with the starch producing the blue-black complex. This complex formation is essentially instantaneous; the result is that the color will suddenly appear. For that reason, this is often referred to as a "clock" reaction – you can (and will) time it with a stopwatch!

Sodium bisulfite will be the source of bisulfite ion, and it is the limiting reactant in all the trials you will conduct. Starch indicator and a small amount of sulfuric acid have been added to that solution, so it may appear cloudy due to the presence of the starch. Potassium iodate solution will be the other reactant.

Experiment Synopsis

Your goal is to determine the order of reaction with respect to iodate ion concentration, so you will carry out the reaction several times, keeping the concentration of bisulfite ion constant (but always well below that of iodate), while varying the concentration of the iodate ion. This will be achieved by reducing the volume of iodate solution. But, in order to maintain consistent reaction conditions, the total volume must be kept constant, so as the volume of potassium iodate used is decreased, an equal volume of distilled water will be added. In each trial, 10.0 mL of the sodium bisulfite-starch-sulfuric acid solution is placed in one test tube, and 10.0 mL of potassium iodate solution is placed in another. The reaction is started by pouring one into the other, then pouring the mixture back and forth twice, rapidly, to ensure mixing. One partner will do the mixing; the other will measure and record the time to the appearance of the blue-black color of the starch-iodine complex. Timing starts at the instant of pouring, and ends when the color suddenly appears. If possible, record times ± 0.1 second, but if such a precise timer isn't available, the sweep second hand on a watch or wall clock will give reasonable results. The following combinations are to be used:

Part A: **Establishing a consistent baseline – All combinations are the same.**

Trial 1: Tube ***a***: 10.0 mL $NaHSO_3$/starch/H_2SO_4 mixture
Tube ***b***: 10.0 mL 0.024 *M* KIO_3
Trial 1 is to be repeated twice more (3 runs total – 1a, 1b, and 1c), using exactly the same combinations.

Part B: **Determining reaction order with respect to iodate ion concentration: $[IO_3^-]$ is varied while $[HSO_3^-]$ is held constant. Each is run only once, although you can repeat any trial for which you feel there's a need to do so.**

Trial 2: Tube ***a***: 10.0 mL $NaHSO_3$/starch/H_2SO_4 mixture
Tube ***b***: 8.00 mL 0.024 *M* KIO_3 + 2.00 mL distilled water

Trial 3: Tube ***a***: 10.0 mL $NaHSO_3$/starch/H_2SO_4 mixture
Tube ***b***: 6.00 mL 0.024 *M* KIO_3 + 4.00 mL distilled water
(See Procedure for special treatment of this combination.)

Trial 4: Tube ***a***: 10.0 mL $NaHSO_3$/starch/H_2SO_4 mixture
Tube ***b***: 4.00 mL 0.024 *M* KIO_3 + 6.00 mL distilled water

Trial 5: Tube ***a***: 10.0 mL $NaHSO_3$/starch/H_2SO_4 mixture
Tube ***b***: 2.00 mL 0.024 *M* KIO_3 + 8.00 mL distilled water

Part C: Investigating the effect of temperature on reaction rate: The combination used for Trial 3 is repeated twice more – once about 10 °C warmer than room temperature, then once about 10 °C cooler than room temperature.

Trial 6: Tube *a*: 10.0 mL $NaHSO_3$/starch/H_2SO_4 mixture
Tube *b*: 6.00 mL 0.024 *M* KIO_3 + 4.00 mL distilled water

Both tubes are warmed in a warm-water bath for 10 minutes to bring both to a temperature that is between 10 and 15 °C above room temperature. The actual reaction temperature will be determined at the end of the trial.

Trial 7: Tube *a*: 10.0 mL $NaHSO_3$/starch/H_2SO_4 mixture
Tube *b*: 6.00 mL 0.024 *M* KIO_3 + 4.00 mL distilled water

Both tubes are placed for 10 minutes in a cool-water bath adjusted to between 10 and 15 °C below room temperature. The actual reaction temperature will be determined at the end of the trial.

Prelaboratory Assignment

1. Read the entire experiment before coming to the laboratory.
2. Prepare a data table in your notebook in which you will record the times for each reaction trial. Note that there are five combinations to be tested, with the first being carried out three times (Trials 1a, 1b, and 1c) to establish consistency of results, and the third being run at three different temperatures. Consult the Experiment Synopsis (above) for the specific combinations to be used.

Prelaboratory Questions

1. The introduction describes the reaction in which bisulfite ion reduces molecular iodine to iodide ions; the other product is sulfate ion. Write and balance the equation for this reaction.
2. Look at the listing of all trials to be conducted, found in the Experiment Synopsis, above. Determine the total amount of each reactant solution you will need. Note that Parts A and C call for repeat trials, so be certain to include all of those.
3. Calculate the initial concentrations (at the instant of mixing) of iodate and bisulfite in each of the combinations (Hint: Only $[IO_3^-]$ changes). Determine the ratio of concentrations of the two principle reactants (ignore the starch and sulfuric acid). What happens to the value of this ratio as you do the ensuing runs? What would you expect to happen to the time needed to consume all of the bisulfite ion? Explain.
4. Although like most generalities, this one leaves a lot to be desired, it is roughly assumed that a 10 °C change in temperature will change the rate of a reaction by a factor of two. You will be testing one of the combinations at three different temperatures, covering a range of about 20 °C. What do you expect to find as the effect of these changes? What change do you expect to see in the times needed for the blue-black color to appear? On a molecular level, why should the times change in the way you predict?

Safety Precautions

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. The mixture of sodium bisulfite, starch, and sulfuric acid is corrosive to skin and clothing. If it gets on your skin, rinse thoroughly with water. For spills on surfaces, wipe up with wet paper towels.
3. Glass thermometers are easily broken. If you are using a mercury-filled glass thermometer, handle it with extreme care! *If it should break, do not deal with the spill yourself. Tell your teacher; she or he will deal with the cleanup.*

2. Chemical splash-protective eyewear must be worn at all times in the laboratory.

Materials

Apparatus

Test tubes, 18 *x* 150 mm or similar[1] (18, if possible)

Graduated cylinders, 10-mL (2)

Plastic transfer pipets (3)

Beakers, 150- or 200-mL, for holding reagent solutions and distilled water

Test tube rack, ideally one that can hold 12 tubes (or more) at one time

Stopwatch[2]

Thermometer

Reagents

Potassium iodate solution, $KIO_3(aq)$, 0.024 *M*

Sodium bisulfite solution, $NaHSO_3(aq)$, 0.016 *M*

Distilled water

Procedure

1. Obtain about 10 mL more than the amounts of the potassium iodate and sodium bisulfite solutions that you calculated in Prelaboratory Question 2.

   Determine in advance which partner will do the timing. It is critical that timing begins at the instant of first mixing and ends when the color of the reaction mixture flashes to blue-black. All of your trials will follow the same three-step procedure; tube ***a*** is always the iodate solution, and tube ***b*** is always the bisulfite mixture.

   1) Pour the contents of Tube ***a*** into Tube ***b***; start timing from the instant of the first pour-over.
   2) Without pausing, pour the mixture back into Tube ***a***, then return it to Tube ***b***. Hold the tube so that the timer can clearly tell when reaction is complete.
   3) The timer stops timing when the dark blue-black color appears.

2. **Special Notes:**

   - **(Trials 1a, 1b, and 1c)** The first combination is to be done three times, to establish consistency of results. If necessary, carry out additional trials until you have three that show good agreement, giving times that span 2.0 second or less (3 seconds or less if using the sweep second hand of a watch or clock).
   - **(Trial 3)** Trials 3, 6, and 7 involve the same combination being run at three different temperatures. As soon as Trial 3 shows the endpoint, insert your thermometer into the tube. Record the temperature of the reaction mixture. Clean your thermometer.
   - It is convenient to prepare several reaction mixtures at once. If you have enough 18 *x* 150 mm test tubes, you could prepare all combinations at one time, but at least try to prepare combinations 1-5 (including the two extras for Trial 1) at one time. You need three beakers – one each for the two reactants plus one for distilled water. You also need separate plastic transfer pipets (or similar) for each. One graduated cylinder is to be used for the iodate solution, the other for the bisulfate mixture. Fill a "***b***" tube with 10.0 mL of the bisulfate mixture for each of the combinations you are preparing. Prepare the "***a***" tubes according to the combinations given in the Experiment Synopsis, above. Use one transfer pipet to add the exact amount of KIO_3 solution called for to the graduated cylinder, and another to add distilled water to the 10.0 mL mark. If you do the tubes in order of descending KIO_3 concentration, little or no significant error is introduced by not cleaning the graduate between fillings.

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[1] The tubes must be large enough to comfortably hold 20.0 mL of combined solutions.

[2] If a stopwatch or other precision timer is not available, the sweep second hand on a wrist watch or wall clock makes an adequate substitute.

- **(Trials 6 and 7)** When setting up your cold-water and warm-water baths, adjust the cooler one to between 10 and 15 °C below the temperature you recorded at the end of Trial 3. Likewise, adjust the warmer bath to a temperature 10-15 °C higher than that temperature. As you did in Trial 3, when the endpoint of each of these trials occurs, measure the temperature of the reaction mixture. Be certain to clean the thermometer between trials.
- If it is necessary for you to clean your tubes between trials, be sure that you dry the tubes, inside and out, to prevent dilution. Follow the instructions given in the Disposal section, below.

3. The solutions, particularly the bisulfite solution, deteriorate over time. If a significant length of time elapses between Part B and Part C (and especially if Trials 6 and 7 are to be done at a later date), it might be a good idea to add a trial that duplicates the room-temperature run of Trial 3, just to establish a new baseline. If these trials are done at a later date, your teacher will probably have to make fresh bisulfite solution, so a room-temperature repeat is definitely in order. A single run should suffice.

Disposal

1. Empty the contents of reaction vessels into a beaker. Add sodium thiosulfate solution just until the blue-black color disappears. This is the signal that all of the molecular iodine has been converted to iodide ion, and is safe to rinse down the drain.
2. Wash the tubes with soap and water, rinse with tap water, followed by a distilled-water rinse and return them to their proper location. If the tubes are to be used again immediately, dry each one, inside and out, to prevent dilution of the reagents in the next trial. If you have access to a source of compressed air, it will speed the drying process.

Analysis and Conclusions

Part A.

1. Average the times that you recorded for the three runs. Calculate the percentage deviation for the three trials.

Part B.

2. Make a plot of initial concentration of iodate (calculated in Prelaboratory Question 3) vs time needed to reach completion[3]. Draw the best smooth curve you can through the data points; they will not form a straight line. This plot and the one that follows should each occupy most of a sheet of the graph paper, found at the end of this manual.
3. Since bisulfite is limiting in each case, calculate the rate of reaction for each combination in $mol \cdot L^{-1} \cdot s^{-1}$, moles HSO3– per liter, using the information from Prelaboratory question 3,. In your notebook, make a table like the one below. Yours will need three more rows than are shown here.

Trial	$[IO_3^-]$ $mol \cdot L^{-1}$	time (s)	Rate $(mol \cdot L^{-1} \cdot s^{-1})$	log $[IO_3^-]$	– log (time)
1 (avg)					
2					

Make a plot of the log of the initial iodate concentration vs –log (time), again using the data from your table. Draw the best-fit straight line through your five data points and calculate its slope. If the points do not appear to form a straight line, make the best straight line you can, using the points that seem to show the most linearity. (Often, the first 3 or 4 combinations fit well, with the fifth being something of an outlier.)

Attach this plot and the one from question 2 to your report when you hand it in.

[3] For Trial 1, use the average time from Question 1, both here and in Question 2.

straight line through your five data points and calculate its slope. If the

4. You are trying to determine the value of *m* in *Equation 10-2*,

$$\text{rate} = k[IO_3^-]^m[HSO_3^-]^n \qquad \textit{(Equation 10-2)}$$

Since the rate of reaction is inversely proportional to the time required for reaction (greater time means a slower rate), then –log (time) corresponds to the rate of the reaction. With $[HSO_3^-]$ held constant in all five combinations, we can lump the specific rate constant, k, and $[HSO_3^-]$ together and replace them with a single term, thus;

$$\text{rate} = C[IO_3^-]^m, \text{ where } C = k[HSO_3^-]^n$$

Replacing rate with $(\text{time})^{-1}$, and taking the common (base 10) logarithm of each side yields

$$-\log(\text{time}) = \log C + m(\log[IO_3^-]) \qquad \textit{(Equation 10-3)}$$

This is the point-slope form of a straight line, and your plot of –log (time) vs $\log[IO_3^-]$ will have a slope equal to *m*, the order of reaction with respect to iodate concentration.

Calculate the slope of your plot from Question 3. What is the order of reaction with respect to $[IO_3^-]$?

Part C.

5. Calculate the rate of reaction, in $\text{mol} \cdot L^{-1} \cdot s^{-1}$, for the two temperatures used in Part C, then use those values and the rate you calculated for Trial 3 to make a plot showing rate as a function of temperature. Be sure to use the actual temperatures (in K) that you recorded on the x-axis of your graph. For this purpose, the quadrille pages of you laboratory notebook will suffice. How well do your experimental results support the "rule of thumb" mentioned above, that the rate of a reaction roughly doubles when the temperature is increased by 10 °C?

Inquiry

You and your partner are to devise an experimental procedure that will enable you to determine the order of the reaction between iodate and bisulfite ions with respect to bisulfite ion concentration. Your plan should include any safety concerns associated with the experiment and should identify the materials to be used.

Describe the data you intend to collect and the calculations that will be carried out, using those data. Address cleanup and disposal of reagents.

Optional – May be assigned if the teacher elects to do so

Once you have determined the order with respect to both reactant concentrations, carry out the following analysis.

1. Using the values obtained for *m* and *n*, and the reaction combinations for trials 3, 6, and 7, determine the value of the specific rate constant, k, at each temperature.
2. Plot *k* as a function of reciprocal temperature, T^{-1}, and draw the best-fit straight line graph among the three points. (Remember that T must be in kelvins!)
3. The slope of your graph has the value, $-\frac{E_a}{R}$, where R is 8.31×10^{-3} $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. Determine the activation energy for this reaction.

Experiment 5

Thin-Layer Chromatography

Experimental Objective

To perform a separation of a mixture of colored organic dyes by thin-layer chromatography and to investigate the effect of varying solvent composition on the effectiveness of the separation.

AP Learning Objective

2.10: The student can design and/or interpret the results of a separation experiment (filtration, paper chromatography, column chromatography, or distillation) in terms of the relative strength of interactions among and between the components.

AP Science Practices

4.2: The student can design a plan for collecting data to answer a particular scientific question.

5.1: The student can analyze data to identify patterns or relationships.

Concepts

Solubility, polarity, qualitative and quantitative analysis

Introduction

The word **chromatography** means "color writing." The name was chosen at the beginning of the 20th century when the method was first used to separate colored components from plant leaves. Over the years, chromatography in its various forms has emerged as one of the most important known methods for the chemical analysis of mixtures.

The earliest form of chromatography, paper chromatography, was performed using ordinary filter paper, which consists primarily of the polymeric carbohydrate cellulose, as the medium upon which the mixture to be separated is applied. The more modern technique of **thin-layer chromatography** (universally abbreviated as **TLC**) uses a thin coating of aluminum oxide (alumina) or silica gel on a glass microscope slide or plastic sheet. The mixture to be resolved is applied to the slide or sheet, then a solvent mixture is allowed to pass through the sample mixture.

In TLC, a single drop or spot of the unknown mixture to be analyzed is placed about half an inch from the end of a TLC slide. The TLC slide is then placed in a shallow layer of solvent mixture in a jar or beaker. Since the coating of the TLC slide is permeable to liquids, the solvent begins *rising* through the coating by capillary action.

As the solvent rises to the level at which the spot of mixture was applied, various effects can occur, depending on the constituents of the spot. Those components of the spot that are completely soluble in the solvent will be swept along with the solvent front as it continues to rise. Components that are not at all soluble in the solvent will be left behind at the original location of the spot. Most components of the unknown spot mixture will lie in between these extremes, and will be carried along by the solvent front, but to *different extents,* reflecting their specific solubilities, allowing them to separate as the solvent front passes. In this way, the original spot of mixture is spread out into a series of spots or bands, with each spot representing one single component of the original mixture.

The separation of a mixture by chromatography is not solely a function of the solubilities of the components in the solvent used, however. The TLC slide coating used in chromatography is not entirely inert to the molecules in the mixture. To one extent or another, the coating material on the slide surface may interact with the molecules of the components of the mixture being separated. Each component of the mixture is likely to have a different extent of interaction with the slide coating. This difference in interaction between the components of a mixture and the support medium forms an equally important

basis for the separation. The coating of the TLC slide adsorbs[1] molecules on its surface to differing extents, depending on the structure and properties of the molecules involved.

In order to quantify a TLC separation, a mathematical function called the **retardation factor**, R_f, is defined by the relationship shown at the top of the next page.

$$R_f = \frac{\text{distance traveled by spot}}{\text{distance traveled by solvent}}$$

The retardation factor depends on what solvent is used for the separation and on the composition of the slide coating used for a particular analysis. Because the retardation factors for particular components of a mixture may vary if an analysis is repeated under different conditions, a *known* sample is generally analyzed at the *same time* as an *unknown* mixture on the same TLC slide. If the unknown mixture produces spots having the same R_f values as spots from the known sample, then an identification of the unknown components has been achieved.

Thin-layer chromatography is only one example of the many different chromatographic methods available. Mixtures of volatile liquids are commonly separated by *gas chromatography*, in which the mixture of liquids is vaporized and passed through a long tube of solid adsorbent material that has been coated with an appropriate liquid. The mixture is pushed along by the action of a carrier gas (usually one that is chemically inert, such as helium). As with TLC, the components of the mixture will have different solubilities in the liquid coating and different attractions for the solid adsorbent material. Separation of the components of the mixture occurs as the mixture progresses through the tube. The mixture components exit the tube one by one and are usually detected by electronic means.

In this experiment, you will perform a thin-layer chromatographic analysis of a mixture of the dyes bromcresol green, methyl red, and malachite green. These dyes have been chosen because they have significantly different retardation factors, so a nearly complete separation should be possible in the appropriate solvent system. Often the components of a mixture are difficulty or impossible to detect with the naked eye, so the TLC slide is coated with a fluorescent indicator. The dyes selected for this experiment have intense, distinct colors, so no special indicator is needed. The chromatographic separation will be attempted in several solvent mixtures to investigate which solvent mixture gives the most complete resolution of the three dyes. In the interest of time and limited hood space, your teacher may assign two or three of the solvent mixtures to individual groups.

In actual practice, thin-layer chromatography has several uses. When a new compound is synthesized, for example, a TLC of the new compound is routinely done to make certain that the new compound is pure (a completely pure compound should only give a single TLC spot; impurities would result in additional spots). TLC is also used to separate the components of natural mixtures isolated from biological systems: for example, the various pigments in plants can be separated by TLC of an extract made by boiling the plant leaves in a solvent. Once the components of a mixture have been separated by TLC, it is even possible to isolate small quantities of each component by scraping its spot from the TLC slide and re-dissolving the spot in some suitable solvent.

Prelaboratory Assignment

Read the entire experiment before you begin.

Prelaboratory Questions

1. What are the two basic factors that lead to separation of mixtures by thin-layer chromatography?
2. Identify at least two methods other than chromatography that involve separating the components of a mixture based on solubility differences.

[1] *Ad*sorb means to stick to the outer surface, as opposed to being *ab*sorbed into a substance.

3. There are four liquids that make up the solvent mixtures that you will use. They are: acetone (CH_3COCH_3), ethanol (CH_3CH_2OH), ethyl acetate ($CH_3COOCH_2CH_3$), and hexane (C_6H_{14}). Draw the Lewis structures for each one and rank them in what you would expect to be the order of increasing polarity. Defend (give reasons for) your rankings. (Hint: You may need to consult your text or some other reference for help with the structures.)
4. You are instructed to wear plastic gloves when preparing the TLC materials for this experiment. Aside from reasons of safety and health, why are gloves needed?

Safety Precautions

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. The organic indicator dyes used in this experiment will stain skin and clothing. Many such dyes are toxic or mutagenic.
3. The solvents used for the chromatographic separation are highly flammable and their vapors are toxic. No flames are allowed in the room while these solvents are in use. Work only in a fume hood or an exceptionally well-ventilated area.
4. Dispose of the solvents in the appropriate waste container. Under no circumstances are they to be poured down the drain.

Materials

Apparatus

Beakers, 200 mL or larger (6)
Plastic TLC slides (~4 x 10 cm)
Latex surgical gloves
Ruler
Pencil
Plastic wrap or Parafilm®
10-microliter (10 µL) micropipets[2]

Reagents

Ethanolic solutions of the indicator dyes:
- methyl red
- malachite green
- bromcresol green

Solvent mixtures: various combinations of:
- Acetone, CH_3COCH_3
- Ethanol, CH_3CH_2OH
- Ethyl acetate, $CH_3COOCH_2CH_3$
- Hexane, C_6H_{14}

Procedure

1. Clean and dry six 200-mL beakers to be used as the chambers for the chromatography and six squares of plastic wrap or Parafilm® to be used as covers for the beakers.
2. Place a small volume of each solvent into separate beakers, to a depth of about 0.5 cm. The mixtures to be used are listed below. Cover the beakers after adding the solvent mixture, and label the beakers with the identity of the mixture each contains.

acetone 60% / hexane 40%	ethyl acetate 60% / hexane 40%
acetone 50% / ethyl acetate 50%	acetone 50% / ethanol 50%
ethyl acetate 50% / ethanol 50%	hexane 50% / ethanol 50%

3. Wearing plastic surgical gloves to avoid any oils transferring from your fingers to the slides, prepare 6 plastic TLC slides by marking *lightly* with pencil (not ink) a line across both the top and bottom of the slide. Do not mark the line too deeply or you will remove the coating of the slide. On one of the lines you have drawn on each slide, mark four small pencil dots (to represent where the spots are to

[2] Glass capillary tubes (both ends open) make an inexpensive substitute.

be applied). *Above* the other line on each slide, mark the following letters: *R* (methyl *r*ed), *M* (*m*alachite green), *G* (bromcresol *g*reen) and *X* (mixture). See Figure 5-1, next page.

4. The spots can be applied using either a 10-mL pipet or by simply dipping a glass melting-point capillary tube into the dye mixture, then touching the tip of the capillary to the slide. Obtain small samples of the ethanolic solutions of the three dyes (methyl red, malachite green, and bromcresol green). Use the micropipet or capillary supplied with each dye, as well for the mixture. Be careful not to mix up the pipets during application of the dyes.

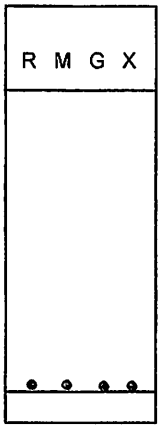

Figure 5–1. Plastic TLC slide with spots of the three dyes and the mixture applied. Keep the spots you apply as small as possible.

5. Apply a single small droplet of the appropriate dye to its pencil spot on each of the TLC slides you have prepared (wipe the outside of the micropipet if necessary before applying the drop to remove any excess dye solution). Keep the spots of dye as small as possible.

6. Apply two droplets of your assigned mixture to the spot labeled *X* (mixture) on each slide, *being sure to allow the first spot to dry before applying the next, so that the spot doesn't become too spread out.* Your assigned mixture may contain one, two, or all three of the indicators being analyzed. Allow the spots on the TLC slides to dry before proceeding.

   Gently lower one of the TLC slides, spots downward, into one of the solvent systems. Be careful not to wet the spots, or to slosh the solvent in the beaker; do not move or otherwise disturb the beaker after adding the TLC slide. Carefully cover the beaker with plastic wrap.

   Allow the solvent to rise on the TLC slide until it reaches the upper pencil line (this will not take very long, about 10-15 minutes). When the solvent has risen to the upper pencil mark, remove the TLC slide and quickly mark the exact location of the solvent front before it evaporates. Mark the TLC slide with the identity of the solvent system used for development. Set the TLC slide aside to dry completely.

7. Repeat the process using the remaining TLC slides and solvent systems. You can easily have more than one system, even all six (if you are to do that many), going at the same time. But if you do, be sure you mark each slide with the solvent system used as you remove each from its development chamber.

8. Determine R_f for each dye in each solvent system and record the values in your notebook. Which solvent system led to the most complete resolution of the dye mixture? Consult with other groups regarding solvent mixtures that you didn't use. If no mixture gave a complete resolution, your teacher may suggest other solvents for you to try, or other proportions of the solvents already used. Save your TLC slides and staple them to the lab report page for this experiment.

Analysis and Conclusions

1. In your notebook, make a table for each solvent system that you used, showing the distance traveled by the solvent front, the distance traveled by each dye and the R_f value for that dye in that particular solvent system.
2. As best you can, determine the R_f value for each of the dyes in the mixture in each of the solvent mixtures. If you cannot distinguish the distance traveled by one or more of the dyes, say so in your report. For those dye/solvent combinations in which you can determine the R_f values, discuss the degree to which the R_f values in the mixture parallel those for the individual dye spots. Would it be possible to use only the R_f values to identify which dye is which in the mixture? Explain.
3. Which solvent mixture gave the *most complete* resolution of the three dyes? Which solvent mixture gave the *poorest* resolution? Which moved up the slide most rapidly? Most slowly?
4. Why is it important to keep the spots applied to TLC slides for chromatography as *small* as possible?
5. Why is it necessary to keep the beaker used for chromatography tightly covered with plastic wrap while the solvent is rising through the TLC slide?
6. TLC slides are most commonly coated with *alumina* or with *silica gel*. Use an outside reference, such as a handbook of chemistry or online source to find out the composition of each of these materials. Make a representation of their structures in you notebook. In what way or ways are their structures similar?
7. In preparing a TLC slide for chromatography, a baseline is drawn *in pencil* for positioning the spots. Why is ink never used for drawing the baseline?
8. Suppose a student placed the dots of colored dye too close to the bottom of the slide. What would be the result?
9. A careless student starts the chromatogram developing, then leaves it alone while working on homework for another class. When the student returns, the solvent front has moved all the way up and off the slide. What can this student expect to find on his slide? How might the determination of an R_f value be affected?

Experiment 6

Intermolecular Forces

Experimental Objective

To use differences in intermolecular forces to distinguish among various types of substances

AP Learning Objective

2.22: The student is able to design or evaluate a plan to collect and/or interpret data needed to deduce the type of bonding in a sample of a solid.

AP Science Practices

4.2: The student can *design a plan* for collecting data to answer a particular scientific question.

5.1: The student can *analyze data* to identify patterns or relationships.

Concepts

Intermolecular forces, variation of solubility with temperature, sublimation, vapor pressure and evaporation

Introduction

Let's be realistic: almost everything we see and deal with on a day-to-day basis consists of mixtures of pure substances, and those pure substances are mostly compounds (excluding air, which is essentially a 4:1 mixture of elemental nitrogen and oxygen). If we want to isolate one of the pure substances from a mixture – a matter of physical change – we have to take advantage of difference in the physical properties of the components of the mixture.

As you know, when substances form homogeneous mixtures (solutions), the particles of one substance must attract, and be attracted by the particles making up the other substance. For heterogeneous mixing, there is no such requirement. Different types of atoms, ions, and molecules exert different types of forces on each other, and particles exerting similar types of forces may do so with greater or lesser effectiveness. In essence, these forces all involve Coulomb's law to one extent or another. Coulomb's law has the form:

$$F = -k\frac{q_1 q_2}{r^2}$$

where q_1 and q_2 are opposite charges, r is the distance between the particles, and k is a proportionality constant. If the signs of q_1 and q_2 are opposite, the minus sign ensures that the force between the particles is positive, meaning they attract one another. If they are both + or both –, then the force will be negative, indicating repulsion. The charges q_1 and q_2 may be formal electrical charges, such as those on ions, they may be the partial positive and negative charges (δ+ and δ–) of permanent dipoles, or they may be the temporary, induced dipoles that cause attraction between nonpolar molecules.

In this experiment, you will make a series of observations of differing behaviors of substances, then look for ways to account for those differences based on the types of intermolecular forces involved.

Prelaboratory Assignment

1. Read the entire experiment before you begin.
2. Review the various types of intermolecular forces (IMF) that individual atoms and ions can exert on one another.

Prelaboratory Questions

1. Identify the various types of intermolecular forces described in your text, ranking them in order of increasing magnitude (weakest to strongest).
2. All substances exhibit dispersion forces. From what do these forces arise, and why does the strength of dispersion forces depend on the number of electrons in the molecule? What is meant by the phrase, molecular polarizability?
3. The equation for Coulomb's Law appears in the Introduction. Strictly speaking, it applies only to the interaction between individually charged objects, but can still be generalized to cover the three types of intermolecular forces, allowing for variations in the proportionality constant, k, and in the rate at which the force strength decreases with distance. For a pair of charged objects, such as a proton and an electron or a sodium ion and a chloride ion, the force is inversely proportional to the square of the distance between the two. Experiments show that dispersion forces, on the other hand, vary inversely as the 6^{th} power of distance:

$$F \propto \frac{1}{r^6}.$$

Given this relationship, explain why substances that have only dispersion forces, such as solid iodine and moth ball materials, have a tendency to pass directly from the solid state to the gas phase.

Safety Precautions

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. In Part B of the procedure, you will be working with boiling-hot water. Protect yourself from burns by using beaker tongs, heat-proof gloves, or hot pads when handling.
3. The liquids used in Part C are all highly flammable. Keep them away from open flames and use only in well-ventilated areas.

Materials

Apparatus

Balance
Hot plate
Sand bath (optional)
Flask, Erlenmeyer or filtering
Beakers: 200- or 250-mL (2)
50-mL (2)
Funnel
Filter paper (2)
Interfaced temperature probes or thermometers (3)
Hand lens (magnifying glass)
Digital interface (CBL2, LabPro, LabQuest, etc.)
Paper towel
Sublimation apparatus (see Figures 6.1a and 6.1b, next page)

Reagents

Orange mixture for Part A
Gray mixture for Part B
Ethanol
Acetone
Hexane or petroleum ether

Procedure

Part A. Sublimation

A.1 Place about 200 mg of the solid mixture in the bottom of a small Erlenmeyer or filter flask. Record the appearance of the mixture. See the figures 6.1(a) and 6.1(b), below.

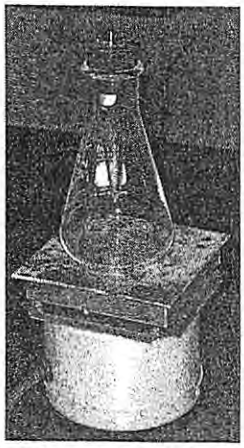

Figure 6.1(a) 5-mL Centrifuge tube with 125-mL Erlenmeyer flask.

Figure 6.1(b) 5-mL Centrifuge tube with 25-mL Filter Flask

A.2 Fill the centrifuge tube with crushed ice, then insert the centrifuge tube into the top of the flask. Note that if you are using a flask that has no side-arm, you do not want a snug fit. You are going to heat the flask gently on a sand bath or hot plate, so this cannot be a sealed system.

A.3 Place the system on the heating apparatus and heat gently. Observe and describe the solid that collects on the centrifuge tube.

Note: **Do not** heat directly with a gas burner for this. If hot plate or sand baths are not available, use a steam bath consisting of a beaker of water on a ring stand and wire screen.

A.4 Once you have made your observations, remove the flask from the hot plate or sand bath and allow it to cool. Gently lift the centrifuge tube from the flask and transfer a few crystals of the solid to a watch glass, petri dish, or other smooth surface, where you can examine them more closely with a hand lens. Enter any additional observations in your notebook.

A.5 Place a small portion of the orange solid remaining in the flask on another area of the watch glass. Use the hand lens to observe and describe the appearance of this solid.

A.6 Return all solids to the flask and add water to a depth of 1-2 cm. Swirl the flask and describe the result.

Part B. Fractional Crystallization.

B.1 Place about 200 mg of the dark gray mixture in a 50-mL beaker and add about 30 mL of water. Heat to near-boiling on a hot plate; try to maintain the temperature for 2-3 minutes, but don't let it come to a full boil. You don't want the volume to decrease too much. What can you say about the solubility of this substance in water? Label your two paper filters "Step B.3" and "Step B.5," respectively. Fold each in fourths, creating a sort of round-bottomed triangle.

B.2 Set up a filtration apparatus (ring stand, iron ring, wire triangle, funnel, "Step B.3" paper filter). Open the filter paper into a cone so that 3 layers are on one side and one is on the other and place it in the funnel; you may find that wetting the filter with a few drops of distilled water makes it stay in place better. Place your second 50-mL beaker beneath the funnel, with the lowest part of the funnel stem just touching the side of the receiver. This helps increase the rate of flow of filtrate through the filter.

See Figures 6.2 and 6.3, next page, for reminders on proper technique for folding filter papers and for filtering suggestions.

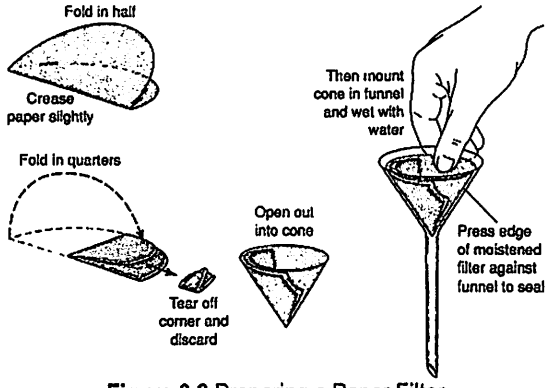

Figure 6.2 Preparing a Paper Filter

B.3 Using a hot pad, gloves, or beaker tongs, filter the mixture of gray-black solid and water. Use a stirring rod to direct the stream of liquid coming from the beaker spout.

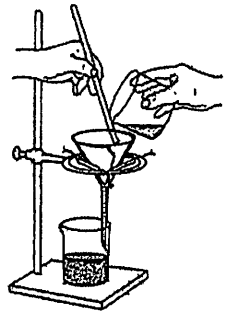

Figure 6.3 Using a Stirring Rod to Guide the stream of liquid.

B.4 Allow the filtrate to cool briefly, then put the receiver containing the filtrate in an ice bath while you remove the "Step B.3" filter containing the residue from your filtration. Set the filter and black residue aside for later examination, then rinse the funnel and insert a second filter, "Step B.5."

B.5 As the previous filtrate cools, new white crystals will be formed, although it may be necessary to scratch the walls of the beaker to induce crystallization. Once crystallization gets started, it goes reasonably fast, and should take only 5-10 minutes.

When it appears that crystallization is complete, and with the beaker and contents at or near 0°C, filter out the white crystals.

Carefully remove the **B.5** filter from the funnel, open the filter, and use a hand lens to examine these crystals and the ones reserved from step **B.4**. In particular, you're looking for similarities and differences between the two solids (in addition to color) that you have recovered in this part of the experiment.

Part C. Evaporation Rates and Intermolecular Forces

C.1 Connect three temperature probes to an interface such as CBL2™, LabPro™, or LabQuest™. Be sure the interface recognizes all three probes. Set the device to collect data at 0.5-second intervals, for a total of three minutes (180 seconds).

C.2 Cut three pieces of paper towel to approximately 4 cm x 5 cm, then roll the towel around each probe with the long side in contact with the probe. Use small rubber bands or rubber rings cut from ¼" latex tubing to fasten the towel to the probe. Leave about 0.5 cm hanging off the end, then twist it.

C.3 Your teacher has prepared small bottles or similar containers with the three liquids to be tested: acetone, ethanol, and hexane. The liquid level in each must be deep enough to wet the entire wrap of paper towel.

C.4 When you're ready, dip all three probes in their respective liquids, remove simultaneously, and press the button or icon to begin data collection. Hold the probes off the lab bench, but hold them steady – try to avoid moving them around, as this creates air currents, which in turn lead to uneven cooling.

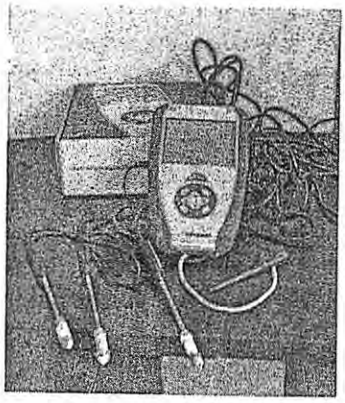

Figure 6.4 Typical Set-up for Part C:
Evaporation Rates and Intermolecular Forces

Analysis and Conclusions

Part A

A.1 The mixture that you used in Part A of this experiment consisted of salicylic acid, the compound from which aspirin is synthesized, and methyl orange, an acid-base indicator similar to phenolphthalein and bromothymol blue. Consult your text for information regarding these two compounds; you may have to check online or in an organic chemistry text to get the structure of methyl orange.

a. Draw the Lewis structures of salicylic acid and methyl orange.

b. Identify the types of intermolecular forces you might expect these two substances to display, both to each other and among themselves.

A.2 Gentle heating causes one of the two substances to sublime (change directly from solid to gas), but had no effect on the other. Which substance sublimed? What does that tell you about the relative strengths of the intermolecular forces between the two compounds?

A.3 Using a molecular model kit, build each of the two compounds to match the Lewis structures you drew in response to question **A.1.a**.

a. Which has the greater number of potential sites for attraction of one molecule to another?

b. Does either of the structures suggest that the attraction may turn out to be intramolecular, with one part of the molecule exerting attractive force on another part of the same molecule? If so, might that explain the answer you gave to question **A.2**?

A.4 What happened when you added distilled water to the recombined mixture? In particular, how do you account for the color you observed?

Part B

B.1 The compounds in the mixture for Part B were charcoal (pure carbon, a complex atomic network solid) and benzoic acid, a molecular solid.

a. Draw the Lewis structure of benzoic acid and identify the parts of the molecule that would exert the most effective intermolecular forces that would make it attractive to water.

b. Based on your observations in Part B, how soluble is benzoic acid in water at room temperature

and below?

c. Again based on your observations, what can you say about the solubility of benzoic acid in water at or near 100 °C?

B.2 The formula for benzoic acid is often written as an abbreviated structural formula, C_6H_5COOH, where the –COOH represents the carboxylic acid functional group. Carboxylic acids are weak acids.

a. What does it mean to say that an acid is "weak?"

b. Write the equation for the dissociation of benzoic acid, using a double arrow ($\rightleftarrows$) to indicate that it is an equilibrium system. Would the dissociated form be more or less likely to dissolve in water? Justify your answer, including both why one form is more likely to dissolve and why the other is less likely.

c. Speculate as to the effect of temperature on the position of the equilibrium between dissociated and undissociated states. Justify your answer based on your knowledge of factors that affect equilibrium systems.

B.3 Your separation was purely qualitative; that is, you were able to show that the benzoic acid could be separated from the carbon (charcoal) by selective crystallization, but you have no way of knowing whether the separation was complete.

a. Based on your observations in this experiment, do you think any of the charcoal dissolved during the heating? Explain.

b. Again using your observations, do you think it likely that not all of the benzoic acid dissolved during heating? Explain.

c. Briefly outline a method by which you could determine the mass percent of each component in the benzoic acid/charcoal mixture.

Part C

C.1 Draw the Lewis structures of the three liquids used in this experiment: ethanol, acetone, and hexane. While the "hexane" that you used was almost certainly a combination of several different structural isomers (molecules with the same combination of elements, but different arrangements of those same atoms), for purposes of this question assume that you used $CH_3(CH_2)_4CH_3$, so-called "normal" hexane, or n-hexane.

C.2 What type or types of intermolecular forces are present in each of the three liquids?

a. ethanol?

b. acetone?

c. hexane?

C.3 The cooling curves that you observed for the three liquids resulted from the evaporation of the liquids from the paper-towel sleeves on each temperature probe. As you know, evaporation is endothermic; in order for a liquid to vaporize, it must absorb heat from its surroundings – this is the same method by which perspiration cools our bodies.

a. Would the liquid with the strongest intermolecular forces have the greatest or the slowest rate of evaporation? Explain.

b. Based on your answers to **C.2**, rank the three compounds in the expected order of increasing strength of intermolecular forces. Justify your answers.

c. Which of the three liquids would be expected to have the greatest rate of evaporation? Which liquid would be expected to have the slowest rate of evaporation?

C.4 Consider the cooling curves for the three liquids in this part of the experiment.

a. Based on the three cooling curves obtained in this experiment, what appears to be the actual order of increasing strength of intermolecular forces? Does this match your predictions from question **C.3**?

b. Account for any differences between your predictions and your actual experimental results.

c. Is it justified to suggest that dispersion forces are always weaker than dipole-dipole forces? Explain.

Summary Questions

1. Question **C.1** mentions that the hexane you used was likely a mixture of several isomers, all with the molecular formula C_6H_{14}, but with different atomic arrangements. In fact, there are five possibilities.
   a. Draw Lewis structures for the five possible arrangements of the atoms, starting with the n-hexane isomer identified in question **C.1**.
   b. Of the five structures, for which would you expect the dispersion forces to be strongest? Weakest? Defend your choices.
2. Nitrogen and chlorine both have an electronegativity of 3.0, but the boiling point for liquid ammonia is –33°C, while the boiling point of hydrogen chloride is –85°C. Suggest an explanation for this observation.
3. In Group 7A, the halogens, fluorine and chlorine are gases, bromine is a liquid, and iodine and astatine are solids at standard temperature and pressure. Account for these observations in terms of the intermolecular forces involved.
4. In group 5A, the nitrogen family, both nitrogen and phosphorus are definitely nonmetallic in their chemistry, arsenic is a metalloid (semi-metal), while antimony and bismuth tend to be metallic. Account for these observations in terms of their atomic structure.

Experiment 13

Le Châtelier's Principle

Experimental Objective

To observe the shifts in equilibrium position predicted by Le Châtelier's principle and to interpret those shifts in terms of the concentration changes involved

AP Learning Objectives

- **6.9** – The student is able to use Le Châtelier's principle to design a set of conditions that will optimize a desired outcome, such as product yield.

AP Scientific Practices

- **SP 4.2** – The student can *design a plan* for collecting data to answer a particular scientific question.

Concepts

Equilibrium systems and Le Châtelier's principle

Introduction

Le Châtelier's Principle describes the effect that applying various types of stress has on the position of a system at equilibrium, that is, whether it will shift to increase or decrease the concentration(s) of products in the equilibrium system. The basic idea that Le Châtelier proposed is that when a system at equilibrium is subjected to a stress, it will shift in such a way as to relieve the effects of that stress.

Stresses include variations in the concentrations of reactants or products, changes in the temperature of the system, and (for reactions involving gases) the pressure. Of these, only a change in temperature actually changes the value of the equilibrium constant.

Most of our investigations occur in open systems, usually in aqueous solution. Unless gases are involved in the reaction, the volume of the system is just the volume of the solution, and pressure is of little or no consequence. This permits us to simplify Le Châtelier's Principle to read: ***For any reaction system at equilibrium in solution:***

> ***if you add a reactant or a product to the system, it will try to consume what was added; if you remove a reactant or a product from the system, it will try to replace what was removed.***

In this experiment you will observe what Le Châtelier's Principle means. The first part of your investigation will deal with two complex ions, both containing cobalt(II); they are $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$. A complex ion consists of a central metal atom, bonded to some number of ions or molecules. These ions or molecules are referred to as ligands. We can represent the shapes of these two cobalt complexes as shown below.

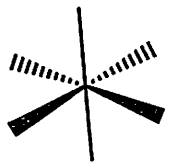

Figure 13.1 (a)

Figure 13.1 (b)

In Figure 13.1 (a), the cobalt(II) ion is at the origin, with the six water molecules at the ends of the bonds. In 13.1 (b), the four chloride ions occupy the ends of the bonds, again with the cobalt(II) ion at the origin.

Subsequent parts of this experiment will involve other systems, but all with the same objective: to understand what stresses were applied, how the system responded, and why it responded as it did.

Prelaboratory Assignment

1. Read the entire experiment before coming to the laboratory.
2. Prepare a three-column table in your notebook with the headings, Action, and System Response. For each of the procedure steps 5-8, as you perform the action called for, write what was done in the "Action" column, and describe what you observe under "System Response." The third column is to be used for any additional notations that you may wish to make, such as any changes that take place between steps B.3 and B.4.

Prelaboratory Questions

1. The formula for solid cobalt(II) chloride is $CoCl_2 \cdot 6H_2O$. What name do we give to compounds which have water molecules bound to them?
2. **a.** Write the equation for dissolving calcium chloride in water.
   b. Use Le Châtelier's Principle to predict the effect of addition of solid calcium chloride to a solution containing both of the cobalt complexes. (See *Equation 13-1* in Analysis and Conclusions.)
3. **a.** Write the equation for dissolving silver nitrate in water.
   b. Write the equation for the precipitation reaction that you would expect when a solution containing silver ions is added to a solution containing chloride ions.

Safety Precautions

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. Cobalt and silver solutions are mildly toxic, so you must wash your hands thoroughly before leaving the laboratory.
3. Silver nitrate will stain skin and clothing. Wipe up all spills with large amounts of water.
4. Concentrated hydrochloric acid will attack skin and clothing. Neutralize acid spills on laboratory surfaces before wiping up.
5. Be careful using the hot plate. Remember that hot surfaces look the same as cool ones. Use a hot pad to transfer hot containers from the hot plate.

Materials

Apparatus

50-mL beaker
Shell vials, 1 dram (5)
Hot plate
Ice bath
Eyedroppers or thin-stem transfer pipets (8-10)
24-well test plate
Microtip transfer pipet or Pasteur pipet (1)
Toothpick (for stirring)

Reagents

cobalt chloride hexahydrate, $CoCl_2 \cdot 6H_2O$
ethanol (or methanol, or 2-propanol)
12 *M* hydrochloric acid, HCl(aq)
calcium chloride pellets, $CaCl_2(s)$
silver nitrate solution, $AgNO_3(aq)$, 0.10 *M*
Ammonia solution, $NH_3(aq)$, 3 *M*
Sodium bromide solution, NaBr(aq), 0.10 *M*
Sodium chloride solution, NaCl(aq), 0.10 *M*
Sodium thiosulfate solution, $Na_2S_2O_3(aq)$, 0.20 *M*

Procedure

Part A. Complexes of Cobalt(II) ion

A.1 Thoroughly dry your 50-ml beaker with a paper towel, then use the markings on the side to measure about 25-30 ml of ethanol into the beaker.

A.2 Examine the solid cobalt(II) chloride, noting both its color and the formula for the compound, as shown on the label of the stock bottle.

A.3 Place a small sample of the solid (about the volume of two drops of water) in the beaker of ethanol and swirl to dissolve the solid. Note the color of the solution.

A.4 Divide most of the solution among five flat-bottomed vials, leaving about 0.5 cm of the solution in the beaker. The actual volume in each vial is not important but the volumes in each should all be approximately equal.

A.5 To one of the vials, add 5 drops of distilled water, one drop at a time, recording observations after each drop. Duplicate the process with each of four other vials, so that all five are the same color. You will use four of the five for Step A.6, retaining one as a control for comparison purposes.

A.6 **a.** Take one of the vials from Step 5 to the fume hood. Use the dropper provided with the acid to CAREFULLY add 5 drops of concentrated hydrochloric acid, one drop at a time, to the solution in the vial.

b. To a second vial from Step 5, add 2-3 small pellets of solid calcium chloride.

c. To the third vial, add 3-4 drops of acetone.

d. To your fourth vial, add 10 drops of 0.1 *M* silver nitrate, $AgNO_3$, one drop at a time.

A.7 Return the contents of your control vial to the beaker containing the remainder of the original alcohol solution of cobalt(II) chloride. Add just enough distilled water to get a color that is about half-way between the blue and pink shades you have observed so far. This solution presumably contains approximately equal amounts of the two complex ions. Place the beaker on a hot plate and warm it until vapors can be seen rising from the surface, about 50°C. Note the change in solution color.

A.8 Finally, chill the beaker in an ice bath, to determine whether the color change in Step A.7 is reversible.

Questions for Part A.

The net-ionic equation for the equilibrium reaction you have been investigating is

$$\underset{\text{pink}}{Co(H_2O)_6^{2+}(aq)} + 4\ Cl^-(aq) \rightleftarrows \underset{\text{blue}}{CoCl_4^{2-}(aq)} + 6\ H_2O(l) \qquad \textit{(Equation 13–1)}$$

1. **a.** Which cobalt complex was favored by addition of water to the solution of cobalt(II) chloride in alcohol?

b. Use Le Châtelier's Principle to explain the color change you observed.

2. **a.** Which cobalt complex was favored in both procedure steps A.6a and A.6b?

b. What ion is common to both of the reagents you used to bring about the color changes in these two steps?

c. Use Le Châtelier's Principle to explain why the color changes occurred in each case.

3. Acetone absorbs water. Use this fact and Le Châtelier's Principle to explain the color change that you saw when you added acetone to the third vial in Step A.6c.

4. Silver chloride, AgCl, is a white solid. The equilibrium constant is $K_{formation} = 6 \times 10^9$ for:

$$Ag^+(aq) + Cl^-(aq) \rightleftarrows AgCl(s) \qquad \textit{(Equation 13–2)}$$

a. At equilibrium, would you expect to have mostly silver and chloride ions in solution, or mostly solid silver chloride? Explain.

b. What color was the precipitate produced in Step 6d? What must it have been?

c. What color did the liquid in the vial turn? Which complex of cobalt was favored? Explain.

d. Use Le Châtelier's Principle to explain why the liquid in the vial underwent the color change.

5. **a.** Which cobalt complex was favored by addition of energy as heat? Which complex was favored by cooling?
   b. For the equation as it appears at the start of this section, $\Delta H = +50$ kJ/mol. Rewrite *Equation 13–1* for the reaction, this time, including the energy term in the equation.
   c. Use Le Châtelier's Principle and the equation from **5b** to explain the color changes that resulted from the heating and cooling.

6. Of the various "stresses" that you applied to the system in this experiment, the only one that actually changes the value of the equilibrium constant is a change in temperature. As you know, an increase in temperature increases the rate of a reaction. For a system at equilibrium, it can be shown that an increase in temperature tends to bring about a greater increase in the rate of the endothermic direction than it does for the exothermic direction. As a solution of cobalt(II) chloride in a mixture of ethanol and water is warmed from 0°C to 50°C, what happens to the concentrations of the two complex ions of cobalt?

Part B: The Copper(II) sulfate – Aqueous ammonia System

B.1 Prepare or obtain 10. mL of a solution of 0.10 *M* copper(II) sulfate, $CuSO_4(aq)$. (More will be used for the Inquiry portion.)

B.2 Obtain 50. mL (preferably in a capped container) of 3.0 *M* aqueous ammonia solution, $NH_3(aq)$, and 5-10 mL of 1.0 *M* sodium hydroxide solution, $NaOH(aq)$.

B.3 Fill each of two 13 *x* 100 mm test tubes with the $CuSO_4$ solution to a depth of about 2 cm (about 2 mL).[1] Using eyedroppers or plastic transfer pipets, add 10 drops of 1.0 *M* $NaOH(aq)$ to one tube, and 10 drops of 3.0 *M* $NH_3(aq)$ to the other. Observe carefully, then set the tubes aside for about 5-10 minutes while you work on the questions for Part B or while you're getting materials together for Part C.

B.4 After the tubes have had a few minutes to settle, note and record the final results, especially any changes that may have occurred.

Questions for Part B

B.1 **a.** Identify the solid that was produced in step B.3. Was the same solid formed in step B.3? Cite evidence from the experiment to support your answer.
b. Write the net-ionic equation for the reaction that takes place in the formation of the solid.

B.2 **a.** Consult a suitable reference, either online or in print, to identify the species that produced the dark blue color seen in Step 5. Cite your reference. (Hint: The colored species is a complex ion.)
b. Write the net-ionic equation for formation of the complex ion.

Part C: Complexes of AgCl and AgBr

C.1 Add 10 drops each of 0.10 *M* sodium chloride, $NaCl(aq)$, and 0.10 *M* sodium bromide, $NaBr(aq)$, to two separate wells of a spot plate or 24-well test plate.

C.2 Add 10 drops of 0.10 M silver nitrate, $AgNO_3(aq)$, to each well and observe (note both the presence of any precipitates and their colors).

C.3 Split the precipitates, keeping track of which halide ion is contained in which well. First, stir the precipitate by placing the tip of a clean microtip pipet on the bottom of the well then expel a gentle squeeze of air to stir the mixture. Take everything up into the pipet and then distribute it drop by drop between the original well and another one next to it.

C.4 Add 4 drops of 3 *M* aqueous ammonia, $NH_3(aq)$, to one half of each precipitate, stir with a toothpick, and observe. Does ammonia cause the precipitate to dissolve?

---

[1] While the specific depth need not be exactly 2.0 cm, the two tubes should be filled to the same depth to make comparison easier.

C.5 Add 4 drops of 0.2 *M* sodium thiosulfate, $Na_2S_2O_3(aq)$, to the second half of each precipitate, stir with a toothpick, and observe. Is there any effect on the precipitate?

Questions for Part C

C.1 While silver chloride and silver bromide solids differ somewhat in appearance, they are nonetheless quite similar. How could information you gained in this part of the experiment be used to more clearly distinguish between the two silver salts?

C.2 In the presence of ammonia, silver forms the complex, diamminesilver, $Ag(NH_3)_2^+(aq)$. In the presence of thiosulfate ion, $S_2O_3^{2-}(aq)$, it forms a complex with the rather scary-looking name, dithiosulfatoargentate(I), $Ag(S_2O_3)_2^{3-}(aq)$. Based on your results in this experiment, answer the following and cite evidence to support your responses.

- **a.** Which forms a stronger bond to the silver cation: chloride, $Cl^-(aq)$, or ammonia, $NH_3(aq)$?
- **b.** Which forms a stronger bond to the silver cation: bromide, $Br^-(aq)$, or ammonia, $NH_3(aq)$?
- **c.** Which forms a stronger bond to the silver cation: chloride, $Cl^-(aq)$, or thiosulfate, $S_2O_3^{2-}(aq)$?
- **d.** Which forms a stronger bond to the silver cation: bromide, $Br^-(aq)$, or thiosulfate, $S_2O_3^{2-}(aq)$?
- **e.** Which forms a stronger bond to silver ions: ammonia, $NH_3(aq)$, or thiosulfate, $S_2O_3^{2-}(aq)$?
- **f.** Which halide ion, chloride, $Cl^-(aq)$, or bromide, $Br^-(aq)$, forms the stronger bond to silver ions?

C.3 If you had a mixed precipitate of $AgCl(s)$ and $AgBr(s)$, how could you separate them?

Inquiry

In Part B, you found that there were two new substances produced when aqueous ammonia was added to a solution of copper(II) sulfate. You and your partner are to design and carry out an experiment to determine whether or not it is possible to produce one of those products without the other, using only the reagents from that part of the Procedure. If it is, you are to determine what conditions make the separation possible.

Your plan should include discussion of safety concerns, plans for disposal of waste, a detailed procedure you expect to follow, the data you plan to collect, and any analysis and calculations that will be involved in your determination.

Consult Chapter 16 of your text. For which of the two products is the *formation* constant greatest? (Hint: Recall that the reaction for formation of a precipitate is the reverse of the process for which the equilibrium constant expression is known as K_{sp}.)

Combine the two formation equations to calculate the value of the equilibrium constant for the reaction system shown below.

$$Cu(OH)_2(s) + 4\ NH_3(aq) \rightleftarrows Cu(NH_3)_4^{2+}(aq) + 2\ OH^-(aq) \qquad \textit{(Equation 13-3)}$$

How can the value of this constant, and Le Châtelier's principle, be used to explain your experimental results? If your experimental results seem to conflict with predictions based on your calculations, look for a way to explain the conflict.

Experiment 14

Titration Curves

A Guided Inquiry Investigation

Experimental Objectives

- To make pH vs volume curves for combinations of strong and weak acids and with a strong base
- To determine the molar mass of an unknown solid acid, using titration data.

AP Learning Objectives

- **1.20** – The student can design, and/or interpret data from an experiment that uses titration to determine the concentration of an analyte in a solution.
- **6.13** – The student can interpret titration data for monoprotic or polyprotic acids involving titration of a weak or strong acid by a strong base (or a weak or strong base by a strong acid) to determine the concentration of the titrant and the pK_a for a weak acid, or the pK_b for a weak base.

AP Science Practices

- **4.2** – The student can *design a plan* for collecting data to answer a particular scientific question.
- **5.1** – the student can *analyze data* to identify patterns or relationships.

Concepts

Strong and weak acids and bases, pH curves, polyprotic acids, buffer systems, hydrolysis of ions

Introduction

Acid-base reactions involving strong acids and strong bases are often referred to as neutralization reactions. The term is valid because at the equivalence point, the numbers of moles of hydrogen ion and hydroxide ion are equal, and the system is neutral, with a pH of 7. Such is not the case for titrations involving weak acids and/or weak bases.

To review, the terms *strong* and *weak* as they are applied to acids and bases, indeed to electrolytes in general, refer to the degree to which the acid or base is present in ionic, rather than molecular form. Strong acids and bases are assumed to be 100% ionized (dissociated), so a 1.0 *M* solution of HNO_3 would be 1.0-molar in hydrogen ion (1.0 *M* H^+) and 1.0-molar in nitrate ion (1.0 *M* NO_3^-), and would contain no undissociated molecules of nitric acid (0.0 *M* HNO_3). Likewise, a 1.0 *M* solution of sodium hydroxide would have 1.0 mole Na^+ and 1.0 mol OH^- per liter of solution, with no NaOH ion pairs present.

The percentage ionization for weak acids, such as acetic acid, $HC_2H_3O_2$, is quite low. A 1.0-molar solution of acetic acid is only 0.4% ionized, so 99.6% of the acid is present as $HC_2H_3O_2$ molecules, with only 0.4% as H^+ and $C_2H_3O_2^-$ ions. The same situation arises with weak bases, such as aqueous ammonia, $NH_3(aq)$: the solution contains mostly ammonia molecules, with very few NH_4^+ and OH^- ions present.

As you know, the conjugate of a weak acid is itself a base, and the weaker acid, the more strongly basic its conjugate will be. Acetate ion, the conjugate of acetic acid, will act as a base in the presence of water. This process is referred to as *hydrolysis*, and is illustrated in *Equation 14-1*.

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftarrows HC_2H_3O_2(aq) + OH^-(aq) \qquad \textit{(Equation 14-1)}$$

In similar fashion, the conjugate acids of weak bases will also undergo hydrolysis. For example, as shown in *Equation 14-2*, ammonium ion, NH_4^+, the conjugate of ammonia, NH_3, will act as an acid, donating a proton to a water molecule.

$$NH_4^+(aq) + H_2O(l) \rightleftarrows NH_3(aq) + H_3O^+(aq) \qquad \textit{(Equation 14-2)}$$

At the equivalence point of a titration involving 1.0 *M* solutions of HNO_3 and NaOH, the only ions present in the system are K^+ and NO_3^-, neither of which undergoes hydrolysis. On the other hand, at the equivalence point for a titration of 1.0 *M* solutions of ammonia, $NH_3(aq)$, and nitric acid, the system would contain equal numbers of moles of nitrate ion, NO_3^-, and ammonium ion, NH_4^+. While the nitrate ion would not interact with water, the ammonium ion would, as shown in *Equation 14–2* and the solution would have a pH below 7, as a result. Similarly, a titration of acetic acid with sodium hydroxide would result in a pH greater than 7 at equivalence, due to the hydrolysis of acetate ion as shown in equation *14–1*.

Sulfuric acid, H_2SO_4, is a typical *diprotic acid*, meaning it has two ionizable (acidic) hydrogen atoms per molecule. Thus, when sulfuric acid is titrated against a strong base such as NaOH, there are two sequential reactions taking place as shown in equations *14–3* and *14–4*. Sulfuric acid is a strong acid, so the net ionic reaction, shown in *Equation 14–3*, is typical of a strong acid-strong base system. Once that reaction is complete, however, and as addition of hydroxide ion continues, there is reaction between hydroxide and the relatively weak acid, bisulfate, HSO_4^-. (See *Equation 14–4*.)

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \textit{(Equation 14-3)}$$

$$HSO_4^-(aq) + H_2O(l) \rightleftarrows SO_4^{2-}(aq) + H_3O^+(aq) \qquad \textit{(Equation 14-4)}$$

In the Skills portion of this experiment, you will carry out two titrations, both following the same basic sequence of steps. Your goal will be to verify the predictions of the preceding paragraphs by titrating 0.10 *M* HNO_3 and 0.10 *M* $HC_2H_3O_2$ with 0.10 *M* NaOH. If you are familiar with the use of pH probes for following acid-base titrations, your teacher may tell you to skip this part, but be sure to read through it, just to refresh your memory and to help you formulate your experimental plan.

If you did Experiment 4, *Analysis of Vinegar*, you recall that it was necessary to standardize the base against a primary standard, potassium hydrogen phthalate, KHP for short. In the present experiment, we are interested primarily in the shapes of the curves of pH vs. volume of titrant, so standardization is not as necessary, but the precise NaOH concentration is needed for the Guided Inquiry that follows, so standardization of the base must be part of your plan.

Prelaboratory Assignment

1. Read the entire experiment before coming to the laboratory.
2. Prepare data tables for each of the titrations to be carried out in Parts A and B. In each case, you will be starting with 30.00 mL of the analyte (the acid). You will need columns for the total volume of base added, starting with 0.00 mL, and for the pH reading following each addition of the base. Even though you may be using an electronic interface that will store all these data for you, you should still keep a written record, since each new titration over-writes the previous one unless you transfer the first titration to a program such as Graphical Analysis. Since these will be tables with only two columns, but many rows, consider making two tables, side-by-side.
3. Answer the Prelaboratory Questions

Prelaboratory Questions

1. Students often forget that the use of KHP to represent potassium hydrogen phthalate can be misleading, that the real molecular formula is $KHC_8H_4O_4$. Calculate the molar mass of KHP.
2. The value of K_a for acetic acid is 1.8×10^{-5}. Use this value to verify the percent ionization for 1.0 *M* $HC_2H_3O_2$ as given in the Introduction. Repeat for 0.10 *M* and 0.010 *M* $HC_2H_3O_2$. Comment on the results of your calculations.
3. Determine the volume of titrant that you expect to need to reach the equivalence point in your titrations for Parts B and C.

Safety Precautions

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. The solutions used in this experiment are corrosive to skin and clothing. Wipe up any and all spills with large volumes of water.

Materials

Apparatus

Erlenmeyer flasks, 125-mL (3)
Buret, 50-mL
pH meter with pH electrode or other interface with pH probe
beaker, 150-mL (3 or 4)[1]
magnetic stirrer and stirring bar(s) (optional)[2]
400-mL (or larger) beaker for rinsing, waste

Reagents

solid potassium hydrogen phthalate, KHP
nitric acid, $HNO_3(aq)$, 0.10 *M*
sodium hydroxide, $NaOH(aq)$, 0.10 *M*
acetic acid, $HC_2H_3O_2(aq)$, 0.10 *M*
solid unknown diprotic acid
distilled or deionized water (wash bottle)

Procedure – Skills

Traditional pH meters, such as the one sketched in Figure 14.1, below, have largely been replaced by smaller, less cumbersome ones, such as the interface shown in Figure 14.2, which appears on the next page, and by hand-held "stick-type" pH probes.

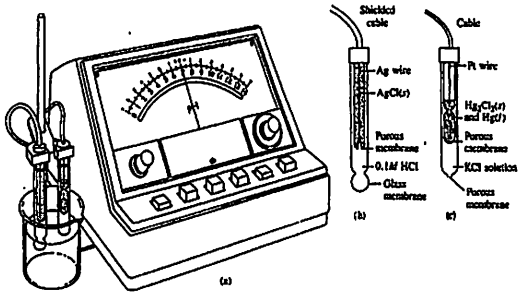

Figure 14.1: A typical, traditional stand-alone pH meter. These are rarely seen any more.

You will begin by standardizing a sodium hydroxide solution, using potassium hydrogen phthalate, the same primary standard that you used in Experiment 4, *Analysis of Vinegar*. You will use the same NaOH solution for the rest of the experiment, including the Guided Inquiry part, which follows this Skills section. If you run out of this NaOH solution before you get to the Inquiry, you will have to repeat the standardization.

The same basic procedure applies to all of your titrations. Before your first titration, rinse the buret twice with distilled water, followed by two rinsings with 0.10 *M* NaOH. Be sure you rinse the tip of the buret, as well as its barrel. Use your large beaker to collect all rinsings. Your teacher will demonstrate the proper technique. After rinsing, fill the buret, including the tip, with 0.10 *M* NaOH. Fill it past the 0.0-mL mark, then carefully run the volume down to between 0.00 and 1.00 mL, read and record the volume present. While it simplifies later volume recording, a reading of 0.00 mL is difficult to attain with high precision.

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[1] Assumes a fresh beaker for each titration, but beakers can be washed between trials. If they are, they should be rinsed with distilled water and dried before the next titration.

[2] If you do not have a magnetic stirrer, you will need to swirl the beaker after each addition of titrant, or use a stirring rod to stir the contents.

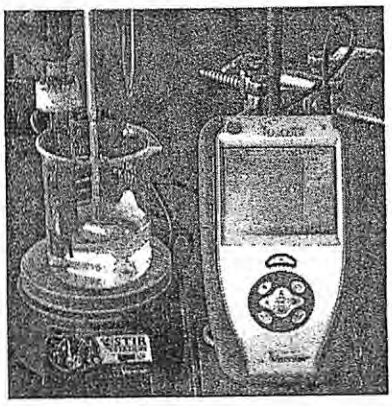

Figure 14.2: Digital Interface with pH probe.

Note that the instructions that follow tell you to manually record pH and total volume of base after each addition of NaOH. If you are using an electronic device (calculator-interfaced, or stand-alone, such as the one shown in Figure 14-2), that information is being stored for you, but you still have to enter the volume of base at each point. See Item 2 of the Prelaboratory Assignment.

Part A. Standardization of NaOH

For this part of the experiment, follow the procedure outlined in Experiment 4 of this manual, using phenolphthalein indicator to identify the equivalence point of each titration. You will not need the pH meter for this part, unless your teacher instructs you to do so.[3]

Part B. Titration of a strong acid with a strong base: HNO_3 and NaOH

B.1 Place 30.0 mL of 0.10 *M* HNO_3 in a clean 150-mL beaker. Place the beaker on the magnetic stirrer, add the stirring bar and begin the stirrer. You may find it necessary to add some distilled water to the beaker to get sufficient depth. This will not affect your results. Carefully lower the pH probe into the solution, taking care to position it so that the tip is not struck by the stirring bar. When the pH reading is stable, note and record the pH of the system for 0.00 mL of base added.[4]

B.2 Add 10.00 mL of 0.10 *M* NaOH from the buret, allow the solutions to mix thoroughly. When the pH is steady, record volume of base added and the pH of the mixture.

B.3 Add 5.00-mL of the NaOH solution. Allow the pH reading to become steady, then record the pH and the total volume of base added, 15.00 mL.

Follow this with five successive 2.00-mL samples of the NaOH, recording the appropriate data after each addition, until a total of 25.0 mL has been added. After each addition, enter the total volume of base.

Now begin to add the base 0.20 mL at a time, recording the total volume of base and the pH after each addition, until the total amount of base added reaches 35.0 mL. Follow with one final 5.00-mL addition and record the final volume and pH.

B.4 Raise the pH probe or electrode out of the solution and use your distilled water wash bottle to rinse it thoroughly, catching the rinsings in the beaker containing your titration products. If you need to re-use your 150-mL beaker, place the contents in your large beaker and reserve it for **Disposal.**

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[3] If you do use the pH meter, be aware that the equivalence point of each titration will be above pH 7 (typically, about pH 9.5), due to the basic nature of the phthalate ion produced, $C_8H_4O_4^{2-}(aq)$.

[4] If you are using a digital interface, it will probably record and store the data for you.

Part C. Titration of a Weak Acid with a Strong Base: $HC_2H_3O_2$[5] and NaOH.

5. Refill your buret, then repeat steps 1-4 starting with 30.0 mL of 0.10 *M* $HC_2H_3O_2$, in place of the HNO_3 used previously. Use the same volumes of base as before, recording the pH as a function of the total volume of base added.

Disposal

1. As you have after each titration, raise the pH sensor out of the titration vessel and use your distilled water wash bottle to rinse it, catching the rinsings in the beaker. After it has been cleaned, consult your teacher as to what you are to do with all electronic equipment.
2. Allow any remaining titrant to drain from your buret into the waste beaker. Since each of your titrations wound up with an excess of NaOH, it is likely (but not certain) that the contents of your waste beaker are basic. Test this by adding a few drops of an indicator such as bromothymol blue or phenolphthalein. If, as expected, the system is basic add small amounts of $HC_2H_3O_2$ (or vinegar) until the color of the indicator changes. The resulting mixture may be rinsed down the drain with large amounts of water.
3. Wash your buret with soap and water, then rinse first with tap water, then with two 5-10 mL portions of distilled water. Clamp the buret above a folded paper towel, with the stopcock open, in an inverted (tip up) position and allow it to drain dry.

Processing The Data

For each of the titrations in Parts B and C, you are to make a separate plot of pH (vertical axis) vs Volume of Titrant (mL) (horizontal axis). In each case, identify the equivalence point for the titration by making a mark on the curve. The equivalence point in each case is the point of inflection. For those cases in which base was being added to acid, it will be where the slope of the graph stops increasing, and begins to decrease. Consult your text for examples.

If you are using a computer-interfaced or calculator-interfaced pH probe, you may have software that will make the plots and identify the equivalence points for you. The same is true if you are using such stand-alone devices as LabQuest™ or PasPort™.

If you are making your own graphs, use graph paper that has at least 10 squares per inch.[6] Draw the best, smooth curve that you can through the data points. A device known as a French curve may be useful for this.

Analysis and Conclusions

1. Make and complete a table with the headings shown at the top of the next page. By "half-equivalence" is meant the point at which you had added half the volume of titrant that was needed to reach equivalence. **Note:** This will *not* necessarily occur at 15.00 mL, and equivalence will not necessarily occur at 30.00 mL of base added.

System	HNO_3/NaOH	$HC_2H_3O_2$/NaOH
Volume of titrant needed to reach equivalence		
pH at equivalence		
Volume of titrant needed to reach half-equivalence		
pH at half-equivalence		

[5] As you may know, acetic acid's systematic name is ethanoic acid, and its formula is often written as CH_3COOH.

[6] The quadrille lines in a typical carbonless laboratory notebook are not precise enough for this purpose. This is particularly true of the carbon copy, the pages you turn in for grading.

2. Write the net ionic equations for each of the two titration reactions that you conducted: HNO_3/NaOH, and $HC_2H_3O_2$/NaOH. (Hint: Consider the species that were present in the acetic acid solution before you began addition of NaOH.)
3. Use the pH values that you recorded to determine the concentration of all ions present in the beaker initially, at half-equivalence, and at equivalence for the titration of nitric acid with NaOH.
4. Repeat the calculations of question 3 for the titration of acetic acid by NaOH.
5. The Henderson-Hasselbalch equation was originally derived for use with buffer systems such as arise so often in biochemistry, but it also describes the effect of concentration on the relationship between pH and pK_a for a weak acid being titrated with a strong base. It has the form

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \qquad \textit{(Equation 14–5)}$$

where $[HA]$ and $[A^-]$ represent the molar concentrations of a weak acid, HA, and its conjugate base, A^-. When your titration of acetic acid with NaOH had reached the half-equivalence point, we can assume that $[HA] = [A^-]$. Explain (a) why this is a valid assumption, (b) what that means for pH and pK_a, and (c) describe the extent to which your experimental result agrees with the predictions made by the Henderson-Hasselbalch equation.

6. In all probability, your experimental results will not exactly match prediction. Whether you got a close match or not, discuss the likely sources of variation from expected behavior that are present in this experiment.

Inquiry

In the Skills portion of this experiment you produced titration curves typical of those found when strong bases are used to titrate strong and weak acids. You also were able to verify – within experimental uncertainty – the predictions of the Henderson-Hasselbalch equation concerning the relationship between pK_a for a weak acid and the pH of the system at the half-titration point. Now you will use what you have learned to establish a procedure to do similar determinations on a compound whose identity is unknown. You will carry out a titration of an unknown solid diprotic acid.

The Challenge. Your goal is to determine the values of K_{a1} and K_{a2} for the acid, and to determine its molar mass. The process is similar to the manner in which you used solid potassium hydrogen phthalate to standardize your sodium hydroxide, but you will probably need to use smaller samples of the solid acid than you did with the KHP. Consult your teacher to be sure, but plan on using sample masses of about 0.20 – 0.25 g. Your plan should include discussion of safety concerns, plans for disposal of waste, a detailed procedure you expect to follow, the data you plan to collect, and any analysis and calculations that will be involved in your determination.

You will be provided with a sample of a solid unknown organic, diprotic acid. The sample will be large enough to permit at least three titrations, if needed. All of the same equipment and materials that you used in the Skills portion of this experiment will be available to you. If possible, you can use the same standardized NaOH solution for your titration(s). The unknown is a relatively weak diprotic acid, so you can expect a situation similar to that described for sulfuric acid in the Introduction, and you can anticipate having two equivalence points. As in the previous titrations, you will monitor the pH of the system as a function of the volume of titrant added.

Assignment. You and your partner are to submit to your teacher a detailed procedure, describing the exact sequence of steps you expect to follow, the data to be collected, and any calculations that will be carried out. Be sure to reference your answer to Analysis and Conclusions question #6 as you develop your strategy for accomplishing your goal. You are to include sections on Safety and Disposal as part of your plan.

You can assume that you will need approximately the same volume of NaOH to reach the second equivalence point of this titration as you needed for the nitric and acetic acid titrations, but that value depends on the sample size of the solid acid used and the actual molar mass of the acid. Since you are working with an unknown, and don't know exactly where the equivalence point will come, consider using smaller increments of titrant (NaOH), especially in the run-up to the first equivalence.

You can use the description in Part A of Experiment 4 as a model on which to design your proposal (potassium hydrogen phthalate is a solid, monoprotic acid). It is recommended that you used between 0.20 and 0.25 grams (± 0.001 g) of the unknown in preparing your acid analyte samples.

Once your teacher has determined that your plan is complete and safe, you will be allowed to conduct your experiment. Note that teacher approval is not a guarantee that your plan will be successful.

Following completion of your experimental procedure, carry out the appropriate calculations to determine: (1) the number of moles of acid in each of your samples; (2) the molar mass of the acid; K_{a1} and K_{a2} for the acid.

Conclude your report by discussing possible sources of experimental error and any suggestions you may have regarding possible modifications of your procedure. In discussing sources of experimental uncertainty, bear in mind that careless or incorrect measurement is not a part of experimental error; those things should not occur.

Experiment 15

Buffers and Buffered Systems

Experimental Objectives

- To learn what buffers are and how they are made
- To see how buffers minimize the pH changes caused by addition of acids or bases to aqueous systems

AP Learning Objectives

- **LO 6.18** – The student can design a buffer solution with a target pH and buffer capacity by selecting an appropriate conjugate acid-base pair and estimating the concentrations needed to achieve the desired capacity.

AP Science Practices

- **SP 2.3** – The student can *estimate numerically* quantities that describe natural phenomena.
- **SP 4.2** – The student can *design a plan* for collecting data to answer a particular scientific question.
- **SP 6.4** – The student can *make claims and predictions about natural phenomena* based on scientific theories and models.

Concepts

Conjugate acid-base pairs, buffers, polyprotic acids.

Introduction

A check of the spice shelf of a well-stocked kitchen may turn up a container labeled "cream of tartar" (chemical name, potassium hydrogen tartrate, $KHC_4H_2O_4$). It is the monopotassium salt of tartaric acid, $H_2C_4H_2O_4$. The structures of tartaric acid, potassium hydrogen tartrate, hydrogen tartrate ion (often called bitartrate), and the tartrate ion may be represented as:

HOOC–CH=CH–COOH
tartaric acid

HOOC–CH=CH–COO$^-$ K$^+$
Potassium hydrogen tartrate

HOOC–CH=CH–COO$^-$
Bitartrate ion

$^-$OOC–CH=CH–COO$^-$
Tartrate ion

As you know, any combination of a weak acid with its conjugate base constitutes a system referred to as a *buffer*. Thus, a combination of tartaric acid and potassium hydrogen tartrate would be a buffer. In fact, since the hydrogen tartrate ion itself can act as an acid, a solution of potassium hydrogen tartrate is a buffer. Here are the first and second dissociation equations for tartaric acid, along with their respective K_a values.

$HOOC\text{-}CH{=}CH\text{-}COOH(aq) \rightleftarrows H^+(aq) + HOOC\text{-}CH{=}CH\text{-}COO^-(aq), \quad K_{a1} = 1.04 \times 10^{-3}$

$HOOC\text{-}CH{=}CH\text{-}COO^-(aq) \rightleftarrows H^+(aq) + {}^-OOC\text{-}CH{=}CH\text{-}COO^-(aq), \quad K_{a2} = 4.55 \times 10^{-5}$

When cream of tartar is added to water, the potassium hydrogen tartrate dissociates totally, producing a solution containing equal amounts of potassium ions, $K^+(aq)$, and hydrogen tartrate (or bitartrate) ions, $HC_4H_2O_4^-(aq)$ ions. Addition of either excess $H^+(aq)$ or $OH^-(aq)$ results in one of the following reactions:

$$HOOC\text{-}CH{=}CH\text{-}COO^-(aq) + H^+(aq) \rightleftarrows HOOC\text{-}CH{=}CH\text{-}COOH(aq), \text{ or}$$

$$HOOC\text{-}CH{=}CH\text{-}COO^-(aq) + OH^-(aq) \rightleftarrows {}^-OOC\text{-}CH{=}CH\text{-}COO^-(aq) .$$

Because the hydrogen tartrate ion, HOOC–CH=CH–COO$^-$, is both the conjugate base of tartaric acid and the conjugate acid of tartrate ion, an aqueous solution of potassium hydrogen tartrate (potassium bitartrate) is itself a buffer.

The same can be said of another familiar household "chemical," baking soda. Baking soda is pure sodium hydrogen carbonate, more commonly known as sodium bicarbonate, $NaHCO_3$. Like the bitratrate ion in cream of tartar, in solution the bicarbonate ion, $HCO_3^-(aq)$, can react with excess hydrogen ion, producing carbonic acid, H_2CO_3, which itself dissociates into water and carbon dioxide and is the cause of the burping that results when antacids containing carbonate or bicarbonate are taken to relieve acid upset. In the presence of excess hydroxide, bicarbonate is converted to carbonate ions and water. This buffer system is important to human beings because it helps to maintain a pH of 7.4 in the body.

In the kitchen, cream of tartar is most often used for making beaten egg whites form and maintain stiff peaks in meringues and frostings, and in combination with baking soda and/or baking powder for leavening of doughs. Cream of tartar is also used in baking; when it is combined with baking soda, $NaHCO_3$, in the presence of water, carbon dioxide is produced, causing cakes to rise.

Baking soda itself is used for causing doughs to rise through CO_2 formation, especially when acidic components, such as buttermilk, are part of the recipe.

In the Skills portion of this experiment you will make and test the properties of several buffer systems. Then in the Inquiry section you will be called upon to make buffers of particular pH and with specified buffering capacity.

Prelaboratory Assignment

1. Read the entire experiment before you begin.
2. Review the concepts and skills you learned in Experiment 14, *Titration Curves*, and review the discussion of buffers and the Henderson-Hasselbalch equation in Chapter 15 of your text.
3. Prepare data tables in your notebook for Parts A and B of the Skills portion of the experiment.
4. To save laboratory working time, calculate the masses of all solid reagents needed (other than NaOH) in Parts A and B of the Procedure.

Prelaboratory Questions

1. The value of K_a for acetic acid is 1.8×10^{-5}. What is the expected pH of:
   a. 0.10 *M* $HC_2H_3O_2$?
   b. 0.10 *M* $NaC_2H_3O_2$?
   c. A solution that is 0.10 *M* in both $HC_2H_3O_2$ and in $NaC_2H_3O_2$?
   d. A solution that is 1.0 *M* in both $HC_2H_3O_2$ and in $NaC_2H_3O_2$?
   e. Account for the answers to parts c and d of this question.
2. The K_a values for phosphoric acid are: $K_{a1} = 7.5 \times 10^{-3}$; $K_{a2} = 6.2 \times 10^{-8}$; $K_{a3} = 4.8 \times 10^{-13}$.
   a. Determine the values of pK_{a1}, pK_{a2}, and pK_{a3}.
   b. Determine the expected pH for 1.0 *M* H_3PO_4.
3. The solution in 2.b is to be titrated with 1.0 *M* NaOH. Let's assume that the hydroxide ion from the titrant will react with the strongest acid available, so that if 50.0 mL of 1.0 *M* NaOH is added to 50.0 mL of 1.0 *M* H_3PO_4, the result will be a 100-mL solution containing 0.050 mol each of $Na^+(aq)$ and $H_2PO_4^-$(aq), and $[Na^+] = [H_2PO_4^-] = 0.50$ *M*. If a second 50.0-mL portion of 1.0 *M* NaOH is now added, the solution will have 0.050 mol of $HPO_4^{2-}(aq)$ in 150. mL, so $[HPO_4^{2-}] = 0.33$ *M*. A final 50.0 mL of base should leave us with 0.050 mol of PO_4^{3-}(aq) in 200. mL of solution, so $[PO_4^{3-}] = 0.25$ *M*.
   a. Determine the expected pH of a solution for which $[H_2PO_4^-] = 0.50$ *M*.
   b. Determine the expected pH of a solution for which $[HPO_4^{2-}] = 0.33$ *M*.
   c. Determine the expected pH of a solution for which $[PO_4^{3-}] = 0.25$ *M*.
4. The introduction states that a solution of sodium bicarbonate is itself a buffer. Write separate net-ionic equations showing how aqueous bicarbonate can react with either excess hydrogen ion or excess hydroxide ion.

Safety Precautions

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. Phosphoric acid is a moderately strong acid. Solutions of sodium hydroxide and sodium phosphate are strongly basic. Avoid contact with skin and clothing, and wipe up all spills with large amounts of water.
3. Wash hands thoroughly with soap and water before leaving the laboratory.

Materials

Apparatus

Beaker, 200-mL (4)

pH meter or interfaced pH probe

Balance, preferably with milligram sensitivity

Reagents

Sodium acetate, $NaC_2H_3O_2(s)$[1]

Acetic acid, $HC_2H_3O_2(aq)$, 1.0 *M*

Acetic acid, $HC_2H_3O_2(aq)$, 0.10 *M*[2]

Sodium phosphate, $Na_3PO_4 \cdot 12H_2O(s)$

Phosphoric acid[3], $H_3PO_4(aq)$, 1.0 *M*

Sodium hydroxide, $NaOH(aq)$, 1.0 *M*

Procedure – Skills

Notes:

a. Solid sodium acetate dissolves endothermically, so significant stirring or swirling may be required.

b. Sodium hydroxide pellets rapidly absorb moisture from the air (they are *deliquescent*). Keep the container tightly closed except when actually removing the pellets.

c. You will be weighing out specified numbers of moles of several solids in this experiment, most of which are hydrates. Be sure to include the waters of hydration when calculating the molar masses of these solids.

Part A. Sodium acetate/acetic acid.

A.1 Add 0.010 mol of solid $NaC_2H_3O_2$ to a 200-mL beaker containing100 mL of 0.10 *M* $HC_2H_3O_2$. Swirl to dissolve the solid completely, test the pH of the system, and set the container aside.

A.2 To a separate 200-mL beaker, add 0.10 mol of solid $NaC_2H_3O_2$ to 100. mL of 1.0 *M* $HC_2H_3O_2$. Swirl to dissolve the solid, then test pH and set the container aside for step 3.

A.3 Add 1 pellet of solid sodium hydroxide (about 0.10 g) to each solution and swirl or stir to dissolve. Test the pH of each, being careful to rinse the pH probe between tests. Record your results.

A.4 Repeat step A.3 with a second pellet of the solid sodium hydroxide. As before, when the solid has all dissolved, test the pH of each solution and record the results.

A.5 Add a third pellet, swirl to dissolve, and again test the pH of each solution.

Disposal for Part A

- Any solution that has a pH between 6 and 8 can be flushed down the drain with copious amounts of water.
- For any solutions whose pH is above 8, add vinegar in small amounts until you have $6 \leq pH \leq 8$, as shown either by the pH probe or by pH test paper.
- For any solutions that show pH below 6, add baking soda, a little at a time, until the system no longer fizzes.

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[1] The hydrated salt, $NaC_2H_3O_2 \cdot 3H_2O$, may be substituted, but it is efflorescent, so effective molar mass may vary and experimental precision may be affected.

[2] You will prepare this by careful dilution of 1.0 *M* stock solution.

[3] Formally, *ortho*-phosphoric acid, or *o*-phosphoric acid. Phosphoric acid is the common name.

Questions for Part A

1. Calculate the numbers of moles of acetate ion and acetic acid molecules in each of the solutions prepared in steps A.1 and A.2. For each solution, determine the initial value of the ratio

$$\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

2. K_a for acetic acid is 1.8×10^{-5}; what is pK_a?

   According to the Henderson-Hasselbalch equation, if $[C_2H_3O_2^-] = [HC_2H_3O_2]$, pH = p$K_a$. Within experimental uncertainty, does your experiment bear out that prediction? (This was also tested in Experiment 14, *Titration Curves*.)

   Assuming that each sodium hydroxide pellet had a mass of about 0.1 g, determine the approximate value for the ratio

$$\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

   after each addition, to each solution. (Note that this calls for six separate ratios, each with only one significant digit.)

3. Account for the changes of pH for each solution, following each addition of solid NaOH.

Part B. Phosphate/hydrogen phosphate/dihydrogen phosphate/phosphoric acid

B.1 Add 0.025 mole of solid sodium phosphate, $Na_3PO_4 \cdot 12H_2O(s)$ to 100. mL of distilled water in a 200-mL beaker. Once the solid has completely dissolved, test the pH of the solution.

B.2 Place 25.0 mL of 1.0 *M* H_3PO_4 in a 200-mL beaker; note and record the pH of the solution.

B.3 To the beaker containing the 25 mL of 1.0 M H_3PO_4, add 25 mL of 1.0 *M* NaOH(*aq*). Mix thoroughly, then measure and record the pH of the system.

B.4 Add a second 25-mL portion of 1.0 *M* NaOH to the container. As before, once everything has mixed completely, note and record the pH of the system.

B.5 Add a third and final 25-mL portion of 1.0 *M* NaOH to the container, mix to dissolve, note and record the pH of the system.

Disposal for Part B

- Follow the guidelines for Part A.

Questions for Part B

1. Your answer to prelaboratory question 2b amounts to a prediction of what you might expect to observe in procedure step B.2.
   a. Within experimental uncertainty, did experiment match prediction? Explain.
   b. Account for any significant difference from this expectation. Based on your results, is the hydrogen ion concentration equal to, more than, or less than 1.0 *M*? Defend your answer.
2. Determine the numbers of moles of NaOH added in each step B.3, B.4, and B.5.
3. Other than water, what were the principal species in solution
   a. in step B.2?
   b. after step B.3?
   c. after step B.4?
   d. after step B.5?

4. Calculate the concentration of the indicated phosphorus-containing ion in solution after each of the following steps:
   a. $H_2PO_4^-$, after step B.3
   b. HPO_4^{2-}, after step B.4
   c. PO_4^{3-}, after step B.5
5. How do your observed pH values compare with those you calculated in Prelaboratory Questions 3a – 3c.? Would you expect your measurements to be the same (within experimental uncertainty) as your calculated values? Why or why not?

Inquiry

You and your partner are to design an experimental plan to produce 100. mL each of two separate buffer solutions, having pH values of 4.50, and 5.00, respectively. Each should be able to maintain its pH within 0.10 pH unit when 5.0 millimoles of excess hydroxide ion or hydrogen ion is added. You will be provided with 1.0 *M* acetic acid, and solid sodium acetate, $NaC_2H_3O_2(s)$. In addition to ordinary laboratory glassware and equipment, you will have access to top-loading electronic balances with milligram sensitivity and common volumetric glassware, including pipets and volumetric flasks.

Your proposal should include the procedure you expect to follow, the data you plan to collect, and any analysis and calculations that were involved in formulating your plan. You are also to include all safety precautions and directions for disposal and cleanup.

Once your teacher has determined that your plan is complete and safe, you will be allowed to conduct your experiment. Note that teacher approval is not a guarantee that your plan will be successful.

Experiment 16

Acids, Bases, and Buffers

Experimental Objectives

- To learn what buffers are and how they are made
- To see how buffers minimize the pH changes caused by addition of acids or bases to aqueous systems

AP Learning Objectives

- **LO 6.20** – The student can identify a solution as being a buffer solution and explain the buffer mechanism in terms of the reactions that would occur on addition of acid or base.

AP Science Practices

- **SP 6.4** – The student can *make claims and predictions about natural phenomena* based on scientific theories and models.

Concepts:

Acids and bases, buffers, strong and weak electrolytes

Introduction

In the Experiment 4, *Analysis of Vinegar*, you used a strong base, sodium hydroxide, NaOH, to determine the concentration of acetic acid in ordinary vinegar. You are going to investigate the same system once again, but this time the indicator will be replaced by a pH meter or with a pH probe connected to an interface. To review, acetic acid is a weak acid; that is, only a very small percentage of the acetic acid molecules are present in ionic form at any one time. The principal species in the solution are acetic acid molecules, not hydrogen and acetate ions. The equilibrium dissociation is a *reversible reaction*, and is represented by a double arrow, and the position of equilibrium lies strongly to the left. Thus:

$$HC_2H_3O_2(aq) \rightleftarrows H^+(aq) + C_2H_3O_2^-(aq) \qquad (Equation\ 16\text{-}1)$$

As discussed in Chapter 14, the pH scale serves as a measure of the concentration of hydrogen ions in an aqueous solution. We represent this concentration by $[H^+]$, with the square brackets understood to refer to the concentration (molarity) of the ion or molecule they enclose. As noted above, acetic acid is a weak acid so relatively few hydrogen ions are present in solution at any given time and the pH is not as low as it would be for a solution of a strong acid, such as hydrochloric acid, HCl, which is 100% dissociated.

Because the acetate ion, $C_2H_3O_2^-$, has a strong tendency to combine with hydrogen ions, the reverse of equation *16-1*, above, we can think of acetate as acting as a base, that is, it acts as a proton acceptor. If you could produce a solution that contained acetate ions without the hydrogen ions, you would expect it to be basic; that is, it should have a pH greater than 7.00. Sodium acetate, $NaC_2H_3O_2$, is a strong electrolyte. It is totally dissociated into ions when dissolved in water.

$$NaC_2H_3O_2(s) \xrightarrow{100\%} Na^+(aq) + C_2H_3O_2^-(aq) \qquad (Equation\ 16\text{-}2)$$

As you might expect (and as you learned in Experiment14), solutions of sodium acetate are mildly alkaline, or basic, due to the tendency of the acetate ions to take a proton from water. This process is known as *hydrolysis*, and represents a state of dynamic equilibrium, as illustrated by equation *16–3*.

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftarrows HC_2H_3O_2(aq) + OH^-(aq) \qquad (Equation\ 16\text{-}3)$$

An interesting type of mixture, which you will investigate in this experiment, is called a *buffer*. Buffers are of two types. An acidic buffer consists of a weak acid, such as acetic acid, mixed with a salt of the conjugate base of the acid (e.g., acetic acid, $HC_2H_3O_2$, and sodium acetate, $NaC_2H_3O_2$, a source of acetate ion, $C_2H_3O_2^-$). A basic buffer consists of a weak base, such as ammonia, $NH_3(aq)$, and a compound that contains the cationic form of the base (in this case, NH_4^+, from a salt such as NH_4Cl).

You will prepare an acidic buffer, consisting of acetic acid and sodium acetate, to see how the buffered system responds when aqueous sodium hydroxide is added. You will compare this result with the behavior you observe when the sodium hydroxide is added to a solution that contains only acetic acid.

In order to help you track the progress of your titrations, you will either use a stand-alone pH meter, or a hand-held interface, such as LabPro™, CBL2™, or LabQuest™. Your teacher will tell you what your instrumentation will be and will direct you as to the proper means to set up, operate, and care for the equipment.

For this experiment, because your primary interest is in the way in which a buffered system behaves differently from one that is not buffered, it will not be necessary to standardize the sodium hydroxide solution, but be aware that the concentration listed for it, 0.10 *M*, is approximate; it is quite reasonable to expect the actual concentration may differ by as much as 5% – 10%, depending on factors such as the extent to which it has been in contact with the air.

Prelaboratory Assignment

1. Read the entire experiment before you begin.
2. Because this experiment uses the same basic set-up as Experiment 14: *Titration Curves*, you should review that experiment, as well. In particular, review the use of potassium hydrogen phthalate.
3. Prepare a Data Table in your notebook in which to record the titration data for Part A; data tables for the later parts can be made as needed.

Prelaboratory Questions

1. Calculate the mass of sodium acetate trihydrate, $NaC_2H_3O_2 \cdot 3H_2O$, you would need to prepare 30.0 mL of 0.10 *M* $NaC_2H_3O_2$ solution. Show your calculations.
2. Acids are proton donors; bases are proton acceptors. In these definitions, the "protons" are actually hydrogen ions. Why are hydrogen ions referred to as protons?
3. a. Acetic acid is a weak acid. Write the Brønsted-Lowry equation for the reaction between water and molecular acetic acid to produce hydronium ions and acetate ions. Identify the conjugate acid-base pairs in your equation.
   b. Ammonia is a weak base. Write the Brønsted-Lowry equation for the reaction between ammonia and water. Identify the conjugate acid-base pairs in your equation.
   c. Would a solution of ammonium chloride, NH_4Cl, be expected to have a pH less than, greater than, or equal to 7.00? Write a chemical equation defending your choice. What are the principal species present in such a solution?
4. Identify the principal species (other than water) present in each of the following systems:
   a. 10. mL of 0.10 *M* hydrochloric acid.
   b. 10. mL of 0.10 *M* sodium hydroxide.
   c. 100. mL of 0.10 *M* acetic acid.
   d. 100. mL of 0.10 *M* sodium acetate.
   e. A combination of systems a. and d.
   f. A combination of systems b. and c.
   g. A combination of systems a, c, and d.
   h. A combination of systems b, c, and d.

Materials

Apparatus

buret, 50-mL
pH meter with pH probe or other interface with pH probe
beaker, 150-mL (2)
magnetic stirrer and stirring bar (optional)[1]
250-mL (or larger) beaker, for rinsing
safety goggles

Reagents

acetic acid, $HC_2H_3O_2$, 0.10 *M*
sodium hydroxide, NaOH, 0.10 *M*
sodium acetate, $NaC_2H_3O_2$, solid
distilled water (wash bottle)
hydrochloric acid, HCl, 0.10 *M*

Safety

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. Sodium hydroxide is corrosive to skin and clothing. Clean up spills with large amounts of water.

Procedure

1. Figure 16.1 shows a typical set up for following the change in pH during titration using an interfaced pH probe. You can use the figure as a guide if you are using the same or a similar device; otherwise follow your teacher's instructions for setting up the titration system.

Figure 16.1: Digital Interface with pH probe.

Part A: Titration of acetic acid by sodium hydroxide[2]

A.1 Rinse the buret twice with a few milliliters of 0.10 *M* NaOH; be sure to rinse the barrel and the tip of the buret. Discard both sets of rinsings in your waste beaker, then fill the buret with fresh NaOH.

A.2 Place 30.0 mL of 0.10 *M* $HC_2H_3O_2$ in the beaker. Place the beaker on the magnetic stirrer and begin the stirrer. Carefully lower the pH probe into the solution, taking care to position it so that the tip is not struck by the stirring bar. Note and record the pH of the solution.

A.3 Add 10.00 mL of 0.10 *M* NaOH from the buret, allow the solutions to mix thoroughly. When the pH is steady, record volume of base added and the pH of the mixture.

Note: While it's desirable to add the exact volumes called for in this and following steps, if you should under- or over-shoot what's called for, be sure to enter the actual volumes used, ± 0.01 mL.

A.4 Add 5.00-mL of the NaOH solution. Allow the pH reading to become steady, then record the pH and the total volume of base added, 15.00 mL. Continue adding two more 5.00-mL samples of the

[1] If you do not have a magnetic stirrer, you will need to swirl the beaker after each addition of NaOH or use a glass stirring rod to stir the contents.
[2] If you performed Experiment 4, *Analysis of Vinegar*, your teacher may instruct you to skip Part A.

NaOH, recording the appropriate data after each addition, until a total of 25.0 mL has been added. After each addition, enter the total volume of base and the observed pH.

Now begin to add the base 1.0 mL at a time, recording the total volume of base and the pH after each addition, until the total amount of base added reaches 35.0 mL. Follow with one final 5.00-mL addition and record the final volume and pH.

Part A Disposal

1. Raise the pH probe from the titration beaker and replace that beaker with your waste beaker. Use the wash bottle to rinse the probe, catching the rinsings in the waste beaker.
2. The contents of the titration beaker is mildly basic, but is safe to rinse down the drain with large amounts of water. Remove the stirring bar, then rinse the beaker well, first with tap water, then with distilled water. It is now ready for use in Part B.
3. Rinse the stirring bar with distilled water. Dry it before re-use.

Part B: Preparing and Titrating the Buffer

B.1 Weigh out the mass of solid sodium acetate you calculated in Prelaboratory Question 1. Place the solid in one of your two 150-mL beakers. Add 30.0 mL of distilled water and swirl or mix until all of the solid has dissolved. (Dissolving is endothermic, so this may take a few minutes; use a magnetic stirrer, if available.)

In your other beaker, dissolve the same mass of solid sodium acetate in 30.0 mL of 0.10 *M* acetic acid. As before, swirl or mix until all of the solid has dissolved. This is the buffer system that you will compare to the unbuffered acid (Part A).

B.2 Use the pH probe to determine the pH of the solution of sodium acetate in distilled water. Record the value. Rinse the pH probe with distilled water, catching the rinsings in your waste beaker.

B.3 Place the beaker containing the acetic acid/sodium acetate mixture on the magnetic stirrer and place the pH probe in the solution, taking care that the stirring bar cannot strike and damage the probe.

B.4 Refill the buret with 0.10 *M* NaOH and titrate the buffer in the same way that you did the acetic acid, steps 4 and 5.

Part B Disposal

1. Follow the instructions for Part A, rinsing all solutions down the drain. Clean the beakers with tap water and distilled water and return them to their proper location.
2. Rinse the stirring bar with distilled water, dry it and return it to its proper location.
3. Drain the buret into your waste beaker. Add a drop of phenolphthalein to the contents of the beaker. If the indicator turns pink, as is likely, add acetic acid, a few milliliters at a time, until the pink just disappears. The contents of the beaker may now safely be rinsed down the drain.
4. Rinse the buret several times with tap water, then with distilled water, being careful to rinse both the barrel and the tip of the buret. Clamp the buret in the inverted position over paper towels so that it can drain.

Part C: Effect of Acid on the buffer.[3]

Note: Rather than having to clean the buret, then refill it with HCl, it is recommended that the 1.0-mL aliquots of HCl be added by a volumetric or Mohr-type pipet. See also the note that follows step C.3.

C.1 Clean your two titration beakers as you did after Part A. Fill one with 30.0 mL of distilled water and the other with 30.0 mL of buffer mixture, prepared in the same way as you did for Part B.

[3] If you performed Experiment 15, *Buffers and Buffered Systems*, your teacher may instruct you to skip Part C.

C.2 To the beaker containing the buffer from step C.1, add 1.0 mL of 0.10 *M* HCl; read and record the pH. Repeat four more times, for a total of 5.0 mL of the strong acid. Rinse the probe thoroughly.

C.3 Repeat step C.2 using the beaker of distilled water from step C.1. As before, read the initial pH, then add 1.0 mL of 0.10 M HCl, up to a total of 5.0 mL of the acid, reading and recording the pH after each addition.

Note: If you are using deionized water rather than distilled water, it is possible that its pH will not be 7.00. In removing metal cations, many ion-exchange columns replace ions such as calcium and magnesium with hydrogen ions. This leads to a pH that is less than 7.00, as would absorption of carbon dioxide from the air, for water that hasn't been freshly distilled.

Part C Disposal

8. If the pH of the solution in your beaker is between 6 and 8, it can be rinsed down the drain with excess water. If it is below 6, add 0.10 *M* NaOH, a little at a time, until the system is in the desired range. This should take very little of the base, so add the NaOH only in small quantities.
9. Return the pH apparatus to the location designated by your teacher.

Analysis and Conclusions

1. Plot your data for each of the two titrations (Parts A and B). Take the time to make a smooth curve; part of your grade will reflect the quality of your graph. As you were directed to do in Experiment 14, either use a computer-generated graph or plot it yourself using graph paper that has at least 10 squares per inch; the quadrille pages of your laboratory notebook will not suffice.
2. Describe the difference between the shapes of the graphs for the buffered and unbuffered systems as they are titrated with sodium hydroxide.
3. Account for the effect of small quantities of a strong acid on the buffered system. Why does the pH not change as rapidly for the buffer as it did for distilled water? What species was consuming the acid?
4. Write net-ionic equations for:
   a. the reaction that occurred in the titrations in Part A and B. (Hint: it is the same reaction in both cases.)
   b. the reaction that occurred when HCl was added to the buffer in Part C.
5. At what pH did the sign of the slope of your graph for Part A change from (+) to (–)? This is known as the *inflection point* of the curve and it is the equivalence point for the titration. Account for the fact that this point is not at pH 7. What were the principal species in the solution at that point? (See the Addendum, below.)
6. At what pH did the sign of the slope of your graph for the titration of the acetic acid—sodium acetate buffer appear to change from (+) to (–)? Account for your result. What were the principal species in the solution at that point?

Addendum

An elegant way to determine the inflection point, one that can be done on a graphing calculator, is to plot the first derivative of pH as a function of volume of base. This results in a curve that shows a spike. You may be able to do this on a computer using a program such as Graphical Analysis™ (Vernier Scientific).