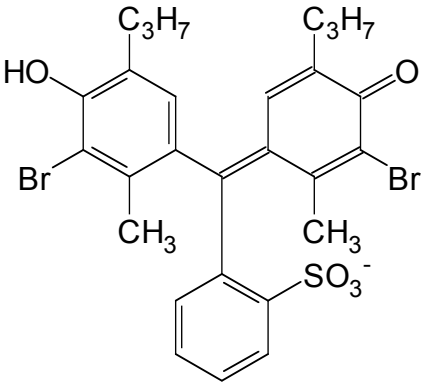
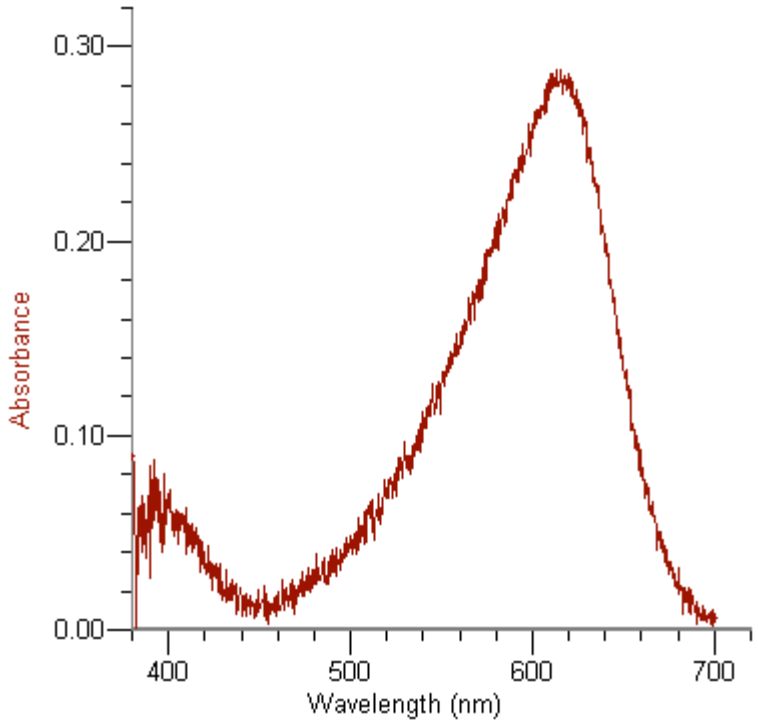
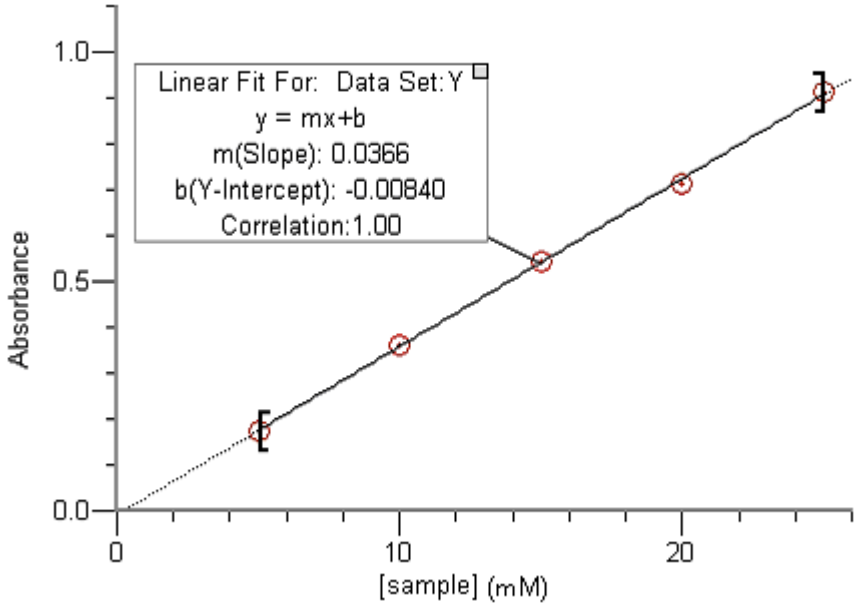
Chem 260 Lab Manual

Fall 2012







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General Policies

Importance of Laboratory Work. Chemistry is an experimental science; experience working in the laboratory, therefore, is essential to almost all chemistry courses. In the lab chemists develop methods to:

- identify unknown substances or to identify the components of a mixture (also known as a qualitative analysis)
- obtain the concentration of one or more species in a sample (also known as a quantitative analysis)
- synthesize new compounds with interesting and useful properties
- determine the chemical and/or physical properties of individual chemical species or of mixtures of chemical species

The particular foci of the laboratory portion of this course are quantitative methods of analysis and investigating the thermodynamic, equilibrium and kinetic properties of chemical reactions.

Another important goal for this semester is to appreciate how chemists work and think and the laboratory is the ideal place to do this. During the semester you will learn to:

- measure mass and volume with appropriate precision and accuracy
- use several routine quantitative methods of analysis, including titrimetry and spectrometry
- design and carry out experiments of your own design
- critically evaluate experimental data and to responsibly report experimental data
- work as part of a small research team

Text. There is no formal text for this lab course. Relevant materials for each lab and additional miscellaneous documents are included in this manual. At times you may find other resources, such as your textbook or the *CRC Handbook of Chemistry and Physics*, to be of use. You also should expect to use the library and the internet to search for information as well.

Laboratory Notebook. Experimentation is the framework on which we construct our knowledge of chemistry. A proper framework, of course, must have a foundation and in chemistry that strong base is the laboratory notebook. A chemist's laboratory notebook is his or her personal journal describing the experimental procedures and observations from which that knowledge is constructed. Our collective confidence in chemistry is built upon experimentation that is well documented. For this reason you will maintain a journal of your work in lab. Unlike your previous chemistry courses, however, you will not use a permanently bound notebook. Instead, you will use an electronic notebook consisting of a Word document with links to electronic data files.

Lab Reports. You will present the results of your work in lab through a series of written reports prepared as a group. Some of these reports will be brief and others will be more detailed. Specific requirements for each experiment are provided elsewhere in this manual.

Grading. Each of the four preliminary experiments is worth 25 points and the four open-ended projects are worth 100 points each. Pre-lab quizzes, one at the beginning of each new experiment, are worth 5 points each. The work you complete as a group must include equal contributions from each student; anyone contributing less than his or her fair share will receive a proportionally lower final laboratory grade at the end of the semester. You will be asked at the end of the semester to provide a frank evaluation of the contributions made by your lab partners.

Policy on Late Lab Reports. Due dates are intended to keep you from falling behind in your work. Because I value thoughtful, well-written work more than absolute deadlines, these due dates usually are intentionally flexible. Unless otherwise specified, there is no penalty for turning work in late if I am still in the process of grading the assignment; however, once I finish grading a set of assignments, any missing work receives a grade of zero—there are no exceptions to this policy. Flexibility in due dates is not a license to procrastinate and abuse of this policy will result in your loss of this privilege. To take advantage of this policy you must consult with me before the assignment is due and show evidence of having made significant progress. This policy does not apply to drafts, which are due, *without exception*, on or before the stated due date.

Academic Integrity. Although you may make frequent use of external resources (e.g. the internet, the library, other students) when preparing lab reports, it is important that the work you submit represents your understanding of the experiment on which you are reporting. Failure to do this is unethical and a serious breach of academic integrity. Be sure to review DePauw's guidelines for academic integrity, which are included in the Student Handbook; in particular, review the examples of plagiarism. Although often unintentional, plagiarism is nevertheless a serious violation that can result in a significant reduction in your grade for an assignment or for the course.

Be sure to consult with your instructor if you are unsure about any issue concerning academic integrity.

Attendance Policy. Attending lab is a requirement and arriving late is inconsiderate to other members of your group. If attendance become a problem, we will work together to find a suitable solution (which may include a reduction in grade for the lab on which you are working). Nevertheless, there are times when an absence is unavoidable due to illness, athletics, job interviews or other unforeseen events. Because lab work is completed as a group, *all group members should be present when working in the lab*. Please inform your group and your instructor of potential conflicts and then work with your group and instructor to find a mutually agreeable time for making up the lost time in lab. To be respectful of others, please limit your need to miss a regularly scheduled lab time and, if the absence is unavoidable, inform everyone as soon as you know of the conflict.

Making Good Use of Laboratory Time (*A Caution!*). You can complete laboratory experiments in the time available *if you come to lab prepared*. At a minimum you should read the experiment's handout before coming to lab and think through what you need to accomplish during the laboratory period. You also should become familiar with the experiment's instrumentation and software by reading the relevant material on the course's web-site. For multiple-week projects your group should meet between laboratory sessions to evaluate data and to make plans for further work; *this planning and discussion is critical to your success*. Should you find that you are unable to complete lab work in the allotted time, then we will work together to improve you preparation.

Lab Schedule

August 23	Check-in to lab; Introduction to lab
August 30	Preparing Solutions
September 6	Using LoggerPro – Newton's Law of Cooling
September 13	Using the Vernier Drop Counter – Analyzing a Household Product
September 20	Using the Ocean Optics Spectrometer – Absorbance, Beer's Law, and Characterizing an Oscillating Reaction
September 27	Thermodynamics of Hydrogen Peroxide's Decomposition – Week 1
October 4	Thermodynamics of Hydrogen Peroxide's Decomposition – Week 2
October 11	Thermodynamics and Solubility of Calcium Hydroxide – Week 1
October 18	Fall Break – No Lab!
October 25	Thermodynamics and Solubility of Calcium Hydroxide – Week 2
November 1	Determining the Acid Dissociation Constant for a Synthetic and Natural Organic Dye – Week 1
November 8	Determining the Acid Dissociation Constant for a Synthetic and Natural Organic Dye – Week 2
November 15	Investigating the Kinetics of the Bleaching of Dyes – Week 1
November 22	Thanksgiving – No Lab!
November 29	Investigating the Kinetics of the Bleaching of Dyes – Week 2
December 6	Check-out of lab

Safety Guidelines

- **Safety glasses must be worn whenever you are in the lab regardless of whether or not you are working on an experiment.** If you wear prescription glasses you may use them in place of safety glasses; for additional protection safety goggles are available. You may remove your safety glasses when working in the study area.

- Food and drinks are not allowed in the lab. If you bring food or drinks with you, be sure to leave them in the study area.

- Shoes must be worn at all times; sandals or open-toed shoes are not allowed. Long hair should be tied back. Exposure to acids (and other chemicals) may damage your clothes so wearing old clothes is a good idea. Long pants, rather than shorts, are strongly recommended.

- Unauthorized experiments are not permitted. No chemicals or equipment are to be removed from the lab without permission.

- Minimize your exposure to chemicals by using fume hoods when directed, cleaning up all spills immediately and washing your hands after handling chemicals. Gloves are available in lab should you desire them.

- Dispose of all wastes only as directed. If you are unsure of how to properly dispose of a chemical, ask before you dispose of it improperly.

- Immediately report any injuries to the instructor.

- Use good housekeeping practices by keeping your lab bench and community areas (e.g. hoods, balances) clean. At the end of the lab period, clean your entire lab bench with a sponge and water.

- Know where to find and how to use the available safety equipment.

- Many experiments include special precautions in the laboratory handout. It is your responsibility to read the laboratory handout before coming to lab so that you are aware of any specific hazards.

****

I have read and understand these safety rules and agree to follow them:

Name_____Date_____

Tips for Working as a Group

Working with other students as part of a small research team can be a rewarding experience. There is an abundance of evidence in the educational literature that the process of discussing an experiment with others leads to a deeper understanding of both the specific experiment and the broader science underlying the experiment. In addition, working as part of a group is a valuable skill that is increasingly desired by employers, graduate programs and health professionals. Indeed, you will spend much of your professional career working closely with others. An effective group, however, does not happen without some effort on your part. The following tips will help you get more out of this experience.

Choosing Partners. This is your most critical decision. Don't approach this choice by deciding to work with your two closest friends. Instead, consider the following:

- *Who's skills best complement mine?* For example, if you are a good writer, but struggle with calculations, try to include someone in your group who has stronger quantitative skills. If you are "all thumbs" when it comes to lab work, then find someone who is better at manipulating glassware and instruments.

- *Who's background best complements mine?* Although this course does not require Calculus or physics, including in your group someone with experience in these courses helps simply because of his or her greater experience with quantitative material. You might consider, as well, including in your group individuals with experience in Chem 120, Chem 130 and/or Chem 240.

- *Who's schedule best matches mine?* Much of your success in lab actually results from making productive use of time outside of lab. Groups with members who can easily meet to prepare for lab, to analyze data and to write reports, are often more successful than groups whose members can never find time to meet.

Assign Responsibilities. This is your second most important decision. Working as a group can be a chaotic experience if no one knows who is responsible for completing tasks. Who, for example, is responsible for gathering together equipment? Or, who is responsible for searching the library or internet for needed information? Effective groups learn to assign specific responsibilities to each member. One approach, which I strongly urge you to consider adopting, is to assign one group member to each of three roles:

- *Manager* – responsible for organizing all aspects of the group's work, including: arranging for meeting times, explaining the experiment's goals to the group, ensuring that the data obtained in lab meets the group's needs, coordinating the preparation of the final report (when prepared as a group) and meeting with the instructor when questions arise.

- *Technician* – responsible for all technical aspects of the group's work, including: maintaining the group's electronic lab notebook and setting up, calibrating and optimizing the equipment needed for the experiment.

- *Chemist* – responsible for all the "wet" work done in lab, including: weighing out samples, preparing reagents and carrying out analyses.

There are many advantages to this format, the most important of which is having one person take responsibility for ensuring that work is completed. Should you choose to use this organization, be sure to rotate group members through all three positions so that everyone has the opportunity to experience each aspect of lab work and so that no one person dominates the group's efforts.

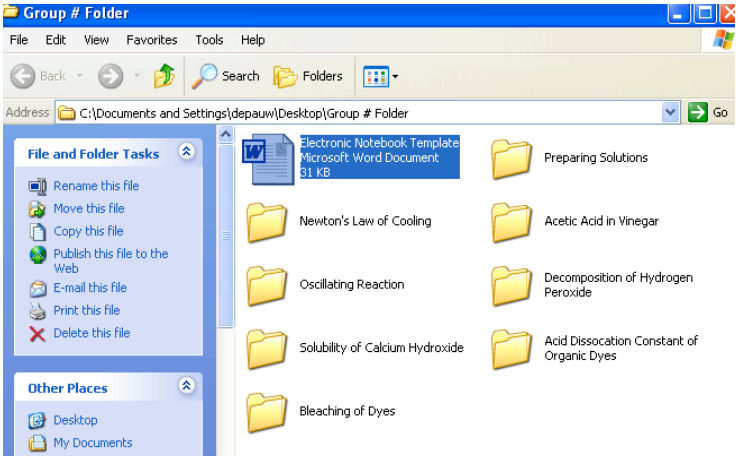
Speak Up When You are Confused and Listen to Each Other. A critical part of working together is ensuring that each group member understands the experiment's goals and how your efforts in lab help accomplish those goals. If you don't understand something, no matter how trivial it seems, then speak up and ask questions. If one member of the group asks a question, then the remaining group members should ensure that the question is answered satisfactorily before continuing; never sacrifice one group member's understanding for the sake of expediency. If you adopt the three roles described above, then the Manager should make sure that everyone understands the experiment.

Be Responsible. By participating in a group you assume responsibility for each other. Remember that your effort affects not just yourself, but it also affects others in your group. When each member of a group lives up to his or her responsibilities, the group's work is inevitably better.

Respect Each Other. Even the best groups will have disagreements. If a disagreement occurs, take a break to cool down and, as a group, try to talk through the problem. Remember to respect and listen to each other

Electronic Laboratory Notebook

Inside your group's workshop folder, which is a shared folder on DropBox, is a copy of your electronic notebook along with folders for each experiment (more on this later).



Your electronic notebook is a Word document that you can open and edit using any computer on campus (either PC or Mac), provided that the computer has access to the campus network and a current copy of Word. This document provides some practical instructions on using your electronic laboratory notebook.

General Philosophy for Maintaining Your Electronic Laboratory Notebook

As with any laboratory notebook, your electronic laboratory notebook must provide an accurate record of your work. At a minimum, your electronic laboratory notebook must contain the following items for each experiment:

- **A Statement of Purpose**: This is a brief statement of the experiment's purpose. Depending on the experiment you may wish to identify the theory or hypothesis being tested (e.g. "The purpose of this experiment is to verify Chicken Little's claim that 'The sky is falling!'.") or the piece of information being sought (e.g. "The purpose of this experiment is to determine the average number of spots on a Dalmatian."). In addition, you may wish to summarize the expected result or indicate how an unexpected result will lead to a different conclusion (e.g. "If we find that the egg's density isn't 19.3 g/cm^3, then we will know that the goose did not lay a golden egg."). *Complete this section before you come to lab.*

- **A Description of Your Planning for the Experiment**: This is a summary of your group's planning for the experiment. Use this section to document your library or internet research and to outline the procedure you plan to follow in lab. The purpose of this section is to outline your procedure so that your time in lab is more productive. Note that this section does not contain data. Thus, you might note that you will need to obtain approximately 0.25 g of dried toadstools, but you

will not record the actual value obtained in lab (which you will enter in a later section). In addition, this section should contain a summary of how you will process your data. *Complete this section before you come to lab.*

- **A List of the Materials and Reagents Used During the Experiment**: This is a brief summary of the equipment and chemicals used during the experiment, which you may write in either a narrative form or as a list. Under the sub-heading of materials list the equipment used, including make and model, and its role in the experiment (e.g. "Soap bubbles were produced using B&B's Big Bubble Blower.") and any hardware and software used to collect and process data. Under the sub-heading of chemicals, all reagents provided to you should be listed (e.g. "A stock solution of 0.10 M Hemlock and freeze-dried Newt's Blood were provided."). Do not list solutions prepared by you in this section; these are recorded with your experimental data and results. You do not need to list commonly available lab supplies, the contents of your lab drawers or distilled water. *Complete this section during lab.*

- **A Comprehensive Record of Experimental Data**: This is the heart of your electronic laboratory notebook as it contains the data collected during the experiment. You may choose to write this as a narrative annotated with data or as a list (e.g. Trial 1…, Trial 2…). Be sure to record all relevant data in an appropriate manner: data for a single analysis may be entered directly; data for a series of related analyses are best entered in tables; and any experimental output from instrumentation can be stored as separate files and identified with filenames in your notebook. All data must be accessible from your electronic notebook. Clarity of presentation is important here as the quality of your written report will depend on your ability to remember what you did in lab. *Complete this section as you do the experiment*.

- **An Analysis of Your Data**: In the process of preparing your group's lab report you will need to analyze your data. For example, you may average the results of several trials to obtain a single value; record this information in your notebook so that you have a record of it (e.g. "The average for the five temperature measurements of Baby Bear's porridge is 48.9^{o}C."). For data that is analyzed using a software program, such as Excel or Graphical Analysis, store the resulting data file in the appropriate folder on the I-drive and identify its filename in this section of your notebook. Feel free to use this section to speculate on the meaning of your data. *Complete this section as you analyze your data.*

You cannot include too much detail or information in your electronic notebook. No one has ever had to repeat an experiment because they recorded too much information in a laboratory notebook!

Because using an electronic notebook is a new experience, the following suggestions and tips will help you take advantage of this format.

Things to Do the First Time You Open Your Notebook

- Scroll to the bottom of the title page and replace the default names with the names of your group's members.
- Agree, as a group, to complete all work using the shared electronic notebook in your workshop folder on the I-drive; this file is your permanent record of all work completed in or out of lab.
- Agree, as a group, to store all relevant data files in your group's workshop folder on the I-drive.

Things to Do Each Time You Open Your Notebook

- The default settings for Word include the formatting and reviewing toolbars. In addition to these, you also will need the outlining toolbar. Add this toolbar by selecting View:Toolbars:Outlining from the main menu.
- Maneuver to the experiment on which you plan to work and click to position the cursor. Ensure that the Outlining toolbar shows that your text is "Body Text", using the pop-up menu if needed.

Things to Do Each Time You Close Your Notebook

- Update your table of contents by clicking on the Update TOC button on the outlining toolbar. On the resulting window, select the option for updating the entire table of contents and select OK.
- Save your notebook to your workshop folder on the I-drive. For safety, you may want to make back-up copies on one or more of your individual P-drives and to the appropriate group folder on your computer's desktop. *One concern when working with an electronic notebook is losing data through accidental deletion or the corruption of files. All files saved on the I-drive are backed up daily by Computing Services and are, therefore, recoverable; however, such requests will take time to process. In addition, after each lab the instructor will back up all group folders to his or her P-drive.*

How to…

- *Enter Superscripts and Subscripts*…Your electronic notebook is preconfigured to make it easy for you to type superscripts and subscripts, both of which are used routinely in chemistry. To type a subscript press Control + 1 followed by your text. For a superscript, press Control + 2 followed by your text. You can resume normal typing by pressing Control + Spacebar.
- *Create Hyperlinks to other Files*…Data collected and stored in other programs, such as LoggerPro, OOIChem or Excel do not need to be copied and pasted into your electronic notebook. Instead, create a hyperlink to the stored file. First, ensure that the target file is stored in your workshop folder on the I-drive. Next, select Insert:Hyperlink… from the main menu. Navigate using the file browser and select your file, which is displayed in both the "address" window and the "text to

display" window. If you desire, you can change the title in the latter window; this is the actual text that will appear in your notebook. You can open any hyperlink by placing the cursor over the hyperlink and pressing Control + Click (in Windows).

- *Make a Table in Word*…To create a new data table select Table:Insert:Table… from the main menu. Enter the number of columns and rows, choose the option for "AutoFit to Contents" and select OK. Place the cursor in the first cell of the first row and begin typing. Use the tab key to move between cells. Additional rows can be added by pressing the tab key when the cursor is in the last cell.
- *Insert a Spreadsheet in Word...*To insert a spreadsheet directly in Word, select Insert: Object… from the main menu. Scroll through the available objects and select Microsoft Excel Worksheet and click OK to insert a fully functioning spreadsheet. If you click outside of the spreadsheet, it reverts to a table. Double-clicking on the table re-opens the spreadsheet.

Analytical Measurements and Techniques

As you work in the laboratory you will make a variety of different measurements. A procedure, for example, may require you to obtain a portion of a solid reagent, dissolve it in a suitable solvent, adjust the pH of the resulting solution to ensure that it is sufficiently acidic, bring the solution to a known volume and measure the solution's absorbance at a wavelength of 450 nm. To accomplish this you must measure the mass of the solid reagent, dissolve the solid, measure the pH of the resulting solution, bring the solution to a known volume and measure the absorbance. Although these instructions may seem straightforward, they actually require you to make some carefully considered decisions about how accurately and precisely you need to determine mass and volume and require an understanding of the instrumentation used to measure pH and absorbance. The next several sections of the lab manual provide important information about making analytical measurements and several common analytical techniques. Topics covered include:

- Accuracy, Precision and Analytical Measurements
- Measuring Mass
- Measuring Volume
- Titrimetry
- Potentiometry
- Visible Absorbance Spectra and Beer's Law

Accuracy, Precision and Analytical Measurements

What are accuracy and precision?

Accuracy is an indication of how close a measurement is to its desired or theoretical value. For example, if we want to dispense 25.0 mL of a liquid reagent, then dispensing 24.9 mL is more accurate then dispensing 25.7 mL. Accuracy usually is reported as a percent error, which we define as

$$\%\ \text{error} = \frac{\text{actual value - desired or theoretical value}}{\text{desired or theoretical value}} \times 100$$

Thus, the accuracies for the two examples cited above are

$$\%\ \text{error} = \frac{24.9 - 25.0}{25.0} \times 100 = -0.4\%$$

$$\%\ \text{error} = \frac{25.7 - 25.0}{25.0} \times 100 = +2.8\%$$

Note that errors affecting accuracy can be either positive or negative.

Precision is an indication of the reproducibility of a set of measurements. Three identically prepared solutions with pH values of 6.76, 6.73, and 6.78, for example, are more precise than three identically prepared solutions with pH values of 6.76, 6.54, and 6.92. Precision usually is reported as a standard deviation, s, which we define as

$$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}}$$

where $\bar{x}$ is the average, or mean result, and x_i is one of the n different results. If you examine this equation closely you will see that a standard deviation essentially is an "average" deviation of the individual measurements from their mean value.[1] Note, as well, that squaring the term in the numerator guarantees that the standard deviation is always positive. As an example, the mean pH for the measurements 6.76, 6.73, and 6.78 is

$$\frac{6.76 + 6.73 + 6.78}{3} = 6.767$$

[1] Note that the standard deviation is not a true average deviation because we divide by one less than the number of measurements ($n - 1$) rather than the actual number of measurements (n). The reason for this is not important to us at this time.

The standard deviation, therefore, is

$$s = \sqrt{\frac{(6.76-6.757)^2 + (6.73-6.757)^2 + (6.78-6.757)^2}{3-1}} = 0.0252$$

Alternatively, we can express the standard deviation as a percent relative standard deviation, s_r, where

$$s_r = \frac{s}{\bar{x}} \times 100$$

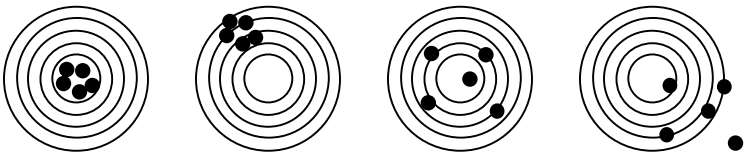
Thus, for the example given above, the relative standard deviation is 0.373%. The standard deviation and relative standard deviation for the other example cited above are 0.270 and 4.00%, respectfully.[1]

Is a pH of 6.76 both more accurate and precise than a pH of 6.8?

Good question. It is tempting to say that a pH of 6.76 is more accurate than a pH of 6.8 because it contains more significant figures, but this is not necessarily correct. In fact, if the instrument used to measure pH is not calibrated, then neither pH reading is accurate. Regardless of its accuracy, we can say that a pH of 6.76 is known more precisely than a pH of 6.8 because the uncertainty for the first measurement is ±0.01 while that for second is ±0.1. The number of significant figures is always an indication of a measurement's precision. If the pH meter has been calibrated properly, then a more precise measurement can lead to a smaller percentage error and, consequently, better accuracy.

If a measurement is accurate, must it also be precise?

Interestingly, the answer to this question is no. As shown by the following targets



there are four possible combinations of accuracy and precision. The target at the far left shows both accuracy and precision as the shots are clustered together (precision) in the target's centermost ring (accuracy). The next example shows results that are precise, due to a tight clustering of the shots, but inaccurate because they are at the target's outer edge

[1] Although you can calculate the standard deviation by hand it is inconvenient to do so when working with large data sets. All scientific calculators and spreadsheets have the ability to calculate standard deviations and averages; learn how to do so with your calculator or favorite spreadsheet. If necessary, you can calculate the relative standard deviation by hand. Because your calculator or spreadsheet will find the average and standard deviation without rounding off intermediate results, values determined by hand will differ slightly from those obtained with a calculator or spreadsheet.

instead of its center. The third example is considered accurate because the five shots cluster around the target's center, but they are not precise because the individual shots are quite far apart from each other. The final example shows a dispersion of shots that is both inaccurate and imprecise. The most interesting thing to note from these examples is that the average of a set of measurements may be accurate even if the individual measurements deviate significantly from the desired or theoretical value.

What factors affect accuracy and precision?

Three main factors affect the accuracy and precision for a set of measurements: the quality of the equipment being used, the ability to calibrate that equipment and the skill of the person using the equipment. These factors are considered further in this section.

The optimum accuracy for any piece of equipment or instrumentation is obtainable only if the equipment is properly calibrated. To calibrate equipment or instrumentation we analyze a system with a known response and either adjust the equipment or instrument to give that response or determine the mathematical relationship between the measured result and its known value. The two examples of accurate target shooting discussed earlier (the targets on the far left and second from the right) require the shooter to calibrate the rifle's scope so that an accurate result is possible. In addition, the potential accuracy of any individual measurement is greater with better quality equipment or instrumentation; the better the scope, the closer each shot will be to the target's center.

Precision, on the other hand, is influenced by both the quality of the equipment or instrumentation and the skill of the person using it. The importance of the user's skill is obvious; when shooting a rifle, for example, a steady hand is a must if a tight, precise pattern of shots is to be achieved. Although less obvious, the quality of the equipment is equally important. The smooth bored muskets used during the Revolutionary War, for example, produced less precise shot patterns than a modern rifle because they lacked grooved bores.

Shouldn't I always strive for the best possible accuracy and precision?

Surprisingly, the answer to this question is a resounding NO. Improving accuracy and precision almost always comes at the expense of time and money. Calibrating an instrument, for example, takes time and the better the quality of the instrument, the more the instrument costs and the less likely it is to be freely available for your use because fewer units are available. You can save a lot of time and aggravation in lab if you learn to make the most accurate and precise measurement possible only when it is absolutely necessary.

So, how do I decide whether a measurement needs to be accurate or precise?

The simplest answer is – if the result of the measurement is to be used in a calculation, then you should try to make the measurement with a suitable level of accuracy and precision. Note the use of the adjective suitable. If your final result must be accurate to within ±1%, then your requirements for the accuracy of an individual measurement needs to be

more stringent than if your final accuracy must be within ±10%. The same observation holds true for precision.

A useful guide to determining how accurate or precise a measurement needs to be is to use significant figures as a guide. For example, if a procedure calls for a 1-L solution of 0.1 M NaCl, then the mass of NaCl obtained and the volume of water used need not be measured in the most accurate and precise way. You can simply measure approximately 5.8 g of NaCl and dissolve it in a 1-L reagent bottle and know that the molarity will be 0.1 to within one significant figure. Or, if a procedure requires that approximately 0.01 g of a reagent be added to each sample, weigh out the first portion to judge the amount and simply add a similar portion to the remaining samples; there is no particular need to weigh out and record each addition. On the other hand, if a procedure calls for a 1.000-L of a 0.1000 M solution of NaCl, then it is necessary to weigh out 5.844 g of NaCl and to use a 1-L volumetric flask to prepare the solution.

When using significant figures as a guide to determining a measurement's appropriate accuracy and precision, be sure that you carefully consider how the value will be used in a calculation. If a procedure calls for a solution of NaCl with a nominal concentration of 0.1 M but the exact concentration is essential when analyzing your results, then you must obtain an accurate and precise mass of NaCl and dilute to volume in a volumetric flask; the exact concentration can then be calculated. Alternatively, you can prepare the solution without regard to accuracy and precision and determine the concentration of NaCl experimentally. Let the procedure from which you are working guide in you making such decisions.

Measuring Mass

The mass of a reagent is determined using a balance. Although there are several types of balances, the most common in the modern chemical laboratory is the electronic pan balance. The sample being weighed is placed on a pan, displacing the pan downward. The balance's circuitry detects this downward motion and supplies an opposing electromagnetic force to counterbalance that from the sample. The magnitude of this force is proportional to the sample's mass. Provided that the balance has been calibrated, an accurate measurement of mass is possible.

Electronic pan balances are available with a variety of precisions (defined here as the number of decimal points to which a sample can be weighed). For most samples a three-digit balance (an uncertainty of ±0.001 g) probably is sufficient, although a four-digit balance (±0.0001 g) may be needed in some cases.

Balances are susceptible to air currents that produce small deflections in the balance's pan and, therefore, cause fluctuations in the recorded mass. This is particularly true for three-digit and four-digit balances. Wind shields are used to minimize this problem. For a three-digit balance the wind shield is a square, plastic wall that fits around the balance's pan with a closable top flap. The shield should be left in place and the top closed if necessary. The balance pan for a four-digit balance is enclosed within a housing with sliding glass doors.

For a solid reagent that is non-hydroscopic (that is, a reagent that does not absorb water), samples can be weighed directly into a suitable container. Because many items of glassware have either small openings that make it hard to directly add solids or have a mass greater than the balance's capacity, samples often are weighed on weighing paper or a weighing boat. In either case, the paper or boat is placed on the balance pan and the balanced is tared so that it registers a mass of 0.000 g. Using a spatula, transfer the desired amount of reagent to the paper or boat. This should be done carefully to avoid spilling reagent on the balance pan as this will give an inaccurate reading.[1] The solid reagent can then be transferred to another container using a small stream of solvent.

For solid reagents that are hydroscopic or that cannot be transferred with solvent, samples must be obtained in a different manner. First, place a portion of the reagent greater than what you need into a small, closed weighing bottle. Weigh the bottle and then transfer a portion of the sample to the appropriate container. Reweigh the bottle and determine the sample's mass by difference.

Liquid reagents also can be weighed on a balance, although they are more commonly measured using glassware.

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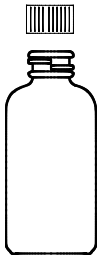
[1] Be sure to clean up any spilled reagents as they may corrode the balance's mechanism and prevent it form working properly. Chemicals spilled on the benchtop should, of course, be cleaned up as they pose a hazard to others working in the lab.

Measuring Volume

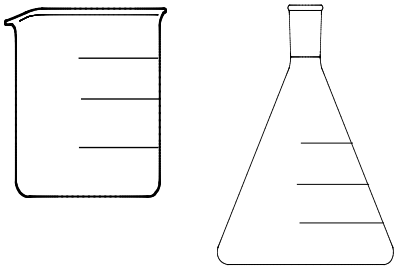
Chemists use a variety of glassware to measure the volume of reagents. The specific type of glassware to use in any situation depends on how accurately or precisely you need to know the volume. In general, glassware is divided into two broad categories: glassware for approximate measurements and glassware for accurate and precise measurements.

Glassware for Approximate Measurements

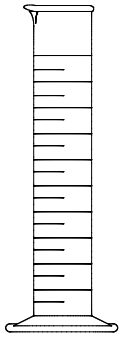
Five common types of glassware are used for the approximate measurement of volume: reagent bottles, beakers, Erlenmeyer flasks, graduated cylinders and disposable pipets. Reagent bottles (shown at right) are the least accurate as they seldom have any marks to indicate approximate volume. Adding 0.1 moles of a reagent to a 1-L bottle and adding water to the top of the bottle's rounded shoulder will produce a solution that is approximately 0.1 M.



Beakers and Erlenmeyer flasks (shown below on the left) usually have several graduation marks on their sides. These marks are accurate to within ±10% of the flask's maximum volume. For example, adding water to the 100 mL mark on a 250-mL beaker will yield a net volume between 75 mL and 125 mL.



A graduated cylinder (pictured at right) provides a more accurate measure of volume than a beaker or Erlenmeyer flask. Typically, a graduated cylinder is accurate to within ±5% of the cylinder's maximum volume. When delivering 5 mL using a 10-mL graduated cylinder, the actual volume is probably between 4.5 mL and 5.5 mL.



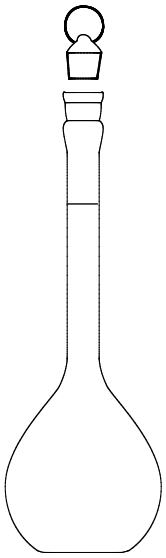
A disposable pipet is a useful way to add a reagent whose volume is given in drops. A common estimate is that 20 drops is approximately equivalent to 1 mL.

In general, the precision for these types of glassware is better than their respective accuracies, although their precision is seldom an issue.

Glassware for Accurate and Precise Measurements

Sometimes we need to be know a reagent's exact volume. When this is the case we worry both about the volume's accuracy (How close is it to 10 mL?) and its precision (How much variation might we expect from one aliquot to the next?). Three types of glassware are commonly used when we need accurate and precise measurements of volume: volumetric flasks, volumetric pipets, and burets. In general, the precision of these types of glassware is better than their respective accuracies.

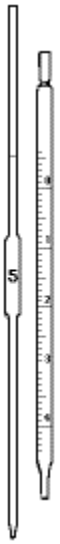
Volumetric Flasks. When filled to its calibration mark, a volumetric flask (shown on the right) contains a specified volume of solution, usually to within ±0.03-0.2% of the stated value, depending on the size of the volumetric flask (although accuracy can be improved through calibration, typically by determining the mass of water contained within the flask and converting to volume using water's known temperature-dependent density). A volumetric flask with a capacity of less than 100 mL generally measures volume to the hundredths of a milliliter, whereas volumetric flasks of 100 mL or greater capacity measure volumes to the tenth of a milliliter. For example, a 10-mL volumetric flask contains 10.00 mL, but a 250-mL volumetric flask holds 250.0 mL. This is an important issue to consider when keeping track of significant figures.



Note the use of the verb ***contain*** in describing the properties of a volumetric flask. This description is important. Although a 100-mL volumetric flask contains exactly 100.0 mL (±0.1 mL), it cannot deliver 100.0 mL to another container. This apparent contradiction results from the fact that you can never completely transfer a liquid from one container to another; some liquid, even if it is only a few drops, remains behind.

Because a volumetric flask contains a solution of known volume, it is useful when preparing a solution whose exact concentration must be known accurately. A known amount of reagent is transferred to a clean volumetric flask and enough solvent added to dissolve the reagent. After dissolving the reagent, additional solvent is added in several portions, mixing the solution after each addition. The final adjustment of volume to the flask's calibration mark is made dropwise using a disposable pipet or a solvent dispensing bottle. To complete the mixing process, the volumetric flask is inverted, shaken and reinverted at least 10 times.

Volumetric Pipets. A volumetric pipet delivers a specified volume of solution. Several different styles of volumetric pipets are available (see pictures to the right), but the most common and the most accurate is a transfer pipet. Transfer pipets consist of a long tube with a bulge in the middle and a single calibration mark (the pipet on the left, for example, is a 5-mL transfer pipet). The accuracy of a transfer pipet is similar to that of a volumetric flask of equal volume; thus, for example, a 100-mL transfer pipet will deliver 100.0 mL of solution (±0.1 mL). As with a volumetric flask, accuracy can be improved by calibrating with water. The other common type of volumetric pipet is a Mohr pipet, which consists of narrow tube with multiple calibration marks (the pipet on the right, for example, is a 5-mL Mohr pipet). The multiple calibration marks allow the user to dispense volumes of variable size; thus a 5-mL Mohr pipet can be used to deliver any specific volume between 0 and 5 mL. In this lab we will make exclusive use of transfer pipets.



Note that a volumetric transfer pipet ***delivers*** a known volume of solution, whereas a volumetric flask contains a known volume. A transfer pipet always contains a volume greater than that delivered. When delivery is complete a small, residual amount of

solution always remains behind. A transfer pipet, therefore, is always contaminated with a small amount of the last solution for which it was used.

Because a transfer pipet delivers a known volume of solution, it is an excellent way to deliver an accurate and precise amount of reagent. To use a transfer pipet, first rinse it with deionized water to remove any traces of the last solution remaining in the pipet. Then, since water is, itself, a contaminant (it will dilute your solution), fill the pipet once with your solution and dispense it to waste. If you have a limited amount of your solution you can partially fill the pipet, seal the top and bottom and rock it back and forth to rinse the pipet's inner surfaces. Any residual amount of solution remaining in the pipet will be similar enough in composition to your original solution such that dilution errors are inconsequential.

To fill a transfer pipet, use suction from a rubber bulb to pull the solution above the pipet's calibration mark (*never use your mouth to suck a solution into a pipet*). Remove the suction bulb and place your fingertip over the top of the pipet. While slowly twisting the pipet, allow the solution's level to drop until it reaches the calibration mark. Wipe the outside of the pipet to ensure that it is dry and to remove any drop of solution clinging to the pipet's tip. Place the pipet over the container in which the solution is to be dispensed. Remove your fingertip and allow the pipet's contents to drain into the container. Touch the tip of the pipet to the container's wall to ensure that the final drop is dispensed. A small, residual amount of solution will remain in the pipet; do not try to force this into the container. Practice this technique until you can confidently use the pipet.

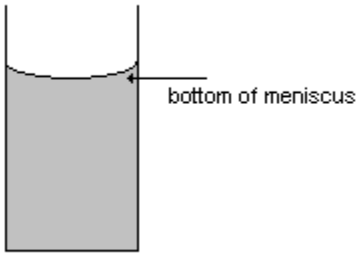
Burets. A buret is used to deliver a variable volume of solution. As shown in the figure on the right, a buret is a long, narrow tube with graduated markings and a stopcock on the bottom end. The topmost mark is labeled with a volume of zero, with additional markings increasing in volume as they go down the buret. The most commonly used buret in the laboratory is a 50-mL buret, which has major markings for every 1-mL increment and minor markings for every 0.1-mL increment. The accuracy of a buret is approximately 0.1% of its total volume; thus, for a 50-mL buret, volumes are accurate to approximately ±0.05 mL.

To use a buret, fill it with solution to a point well above the mark for zero volume. Open the stopcock and allow the solution to flow until the portion of the buret below the stopcock is filled (without any air bubbles) and the volume is below the zero mark. Record this volume as the initial volume. Place a receiving flask below the buret and open the stopcock until the desired amount of solution has been dispensed. Record the final volume and determine the total volume delivered by difference.

Additional Important Details. Two important precautions are needed when working with volumetric pipets, volumetric flasks and burets. First, the volume delivered by a volumetric pipet assumes that the glassware is clean. Dirt and grease on the volumetric pipet's inner surface prevents liquids from draining evenly, leaving droplets of the liquid on the pipet's walls. For a volumetric flask, drops of liquid above the calibration mark mean that the flask contains more than its specified volume. Drops of liquid on a pipet's

wall below the calibration mark mean that the pipet delivered less than its specified volume.

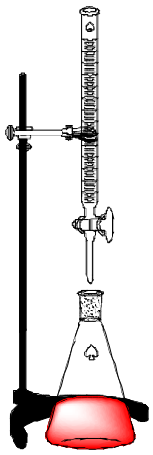
Second, when filling a pipet or volumetric flask, set the liquid's level exactly at the calibration mark. The liquid's top surface is curved into a meniscus, the bottom of which should be exactly even with the glassware's calibration mark. To avoid parallax errors, the meniscus should be adjusted with your eye at the same level as the calibration mark. If your line of sight is from above the calibration mark, for example, then you will tend to overfill the volumetric pipet or volumetric flask. When using a buret, the recorded volumes also are read using the solution's meniscus.



Titrimetry

This brief tutorial describes the basic procedure for conducting titrations in the Chem 260 lab. Although the tutorial makes use of acid/base chemistry, the discussion also applies to other types of reactions.

What is an Acid/Base Titration?



An acid/base titration is an experimental technique in which a solution containing an acid (or a base) is added dropwise to a solution containing a base (or an acid). The solution being added dropwise is called the titrant and the solution to which the titrant is added is called the sample. The sample is normally placed in an Erlenmeyer flask whose size is sufficient to contain both the sample and the added titrant. In addition, it should be possible to swirl the solution without the risk of it sloshing out of the container. The titrant is placed in a buret allowing for its controlled addition to the sample. The figure to the right shows a typical setup.

How is a Titration Used to Determine the Concentration of an Acid or Base?

Suppose, for example, that we have a monoprotic acid, HA, of unknown concentration and a monoprotic base, B, whose concentration is known. When mixed together, the acid and base react according to the following stoichiometry

$$HA + B \rightarrow HB^+ + A^-$$

Let's assume, as well, that the reaction essentially proceeds to completion. If we titrate a solution of B into a sample containing HA until they are mixed in an exact stoichiometric ratio, then we know that

$$\text{moles B} = \text{moles HA} \times \frac{1\,\text{mol B}}{1\,\text{mol HA}}$$

where the ratio on the right-side of the equation accounts for the reaction's stoichiometry. The moles of HA and B can be found from the product of their respective molarities, M, and volumes, V

$$\text{moles HA} = M_{HA} \times V_{HA}$$

$$\text{moles B} = M_B \times V_B$$

and

$$M_B \times V_B = M_{HA} \times V_{HA}$$

As an example, if 36.42 mL of a 0.116 M solution of B completely react with 25.00 mL of HA, then the concentration of HA is

$$M_{HA} = \frac{M_B \times V_B}{V_{HA}} = \frac{(0.116\ \text{M})(36.42\ \text{mL})}{25.00\ \text{mL}} = 0.169\ \text{M HA}$$

If the acid is diprotic, H_2A, and we react it with sufficient B such that both protons are completely consumed, then

$$H_2A + 2B \rightarrow 2HB^+ + A^{2-}$$

$$\text{moles B} = \text{moles HA} \times \frac{2\ \text{mol B}}{\text{mol HA}}$$

$$M_B \times V_B = 2 \times M_{H_2A} \times V_{H_2A}$$

Obviously, there are many other possibilities (diprotic bases, triprotic acids, etc), but the details for such cases follow easily from this description.

Sometimes the acid or base is obtained as a solid. Suppose, for example, that you need to determine the concentration of a monobasic strong base, B, by titrating it against a known mass of a solid monoprotic weak acid, HA. In this case we obtain the concentration of the base using the following equation

$$\text{moles B} = \text{moles HA}$$

$$M_B \times V_B = \frac{g\ \text{HA}}{MM_{HA}}$$

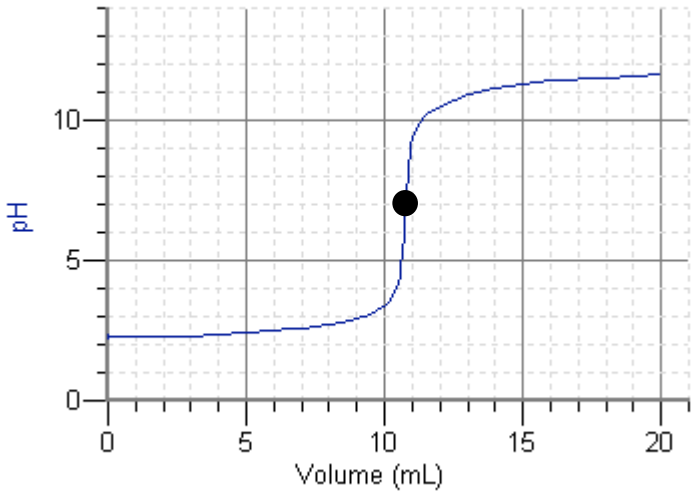
where MM_{HA} is the gram molar mass for HA.

How Do We Know When an Acid and Base Have Been Mixed Stoichiometrically?

When the titrant and sample are mixed in an exact stoichiometric ratio the titration is said to have reached its *equivalence point*. Finding this equivalence point is the key to any titration. There are two general approaches for finding the equivalence point: (1) using a visual indicator that changes color at the equivalence point or (2) measuring the sample's pH as the titrant is added. The use of an indicator is straightforward and needs no detailed discussion (one just adds the titrant dropwise until the indicator undergoes its specified

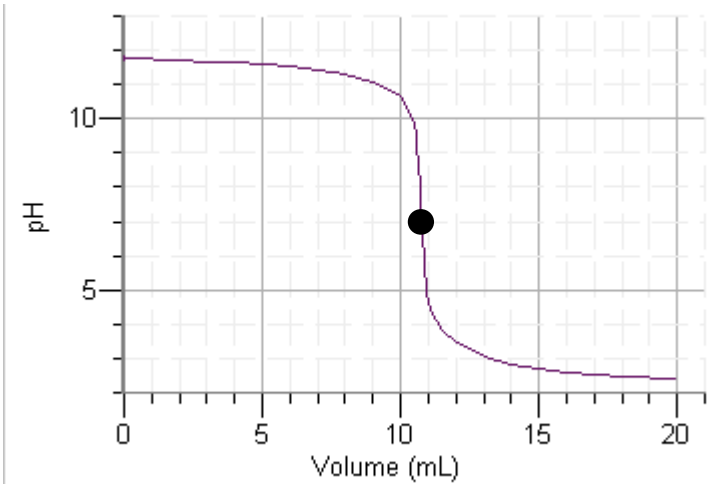
change in color, recording the total amount of titrant needed to reach the equivalence point).[1]

Suppose the sample is a strong acid and the titrant is a strong base. Before adding titrant the sample's pH depends on the strong acid's concentration. Adding titrant causes a slow increase in pH as the strong base neutralizes the strong acid. The rate at which the pH changes becomes greater as the equivalence point is neared, reaching its maximum rate of change at the equivalence point, which in this case occurs when the pH is 7.00. Following the equivalence point, the rate of change in pH becomes smaller, producing a slow, gradual rise in pH. The resulting *titration curve* looks something like the figure shown to the right.



The equivalence point (shown as a ● in the figure to the right) is located visually by finding the point in the steeply rising portion of the titration curve where the rate of change in pH is greatest.

The titration curve for other samples will be similar. When the sample is a strong base and the titrant is a strong acid, for example, then the titration curve will begin at a more basic pH and will end up at a more acidic pH; the general shape, as shown here, is the same. Note that the equivalence point in this case also occurs at a pH of 7.00.



Although the equivalence points in the two examples shown above are both 7.00, this is not always the case. When titrating a weak acid, HA, with a strong base, for example, the pH at the equivalence point will be basic. We can show that this must be true by noting that the reaction

$$HA + OH^- \rightarrow H_2O + A^-$$

[1] To be exact, a visual indicator signals an *endpoint,* not an equivalence point. If the proper indicator is chosen, then the difference between the endpoint and the equivalence point is inconsequential. Selecting an appropriate indicator is a topic that we will not explore in this course.

produces a solution of the weak acid's conjugate weak base, A^-, at the equivalence point. The pH, therefore, must be greater than 7.00. Titrating a weak base with a strong acid will, of course, gives an equivalence point that is less than 7.00.

Automated Titrations

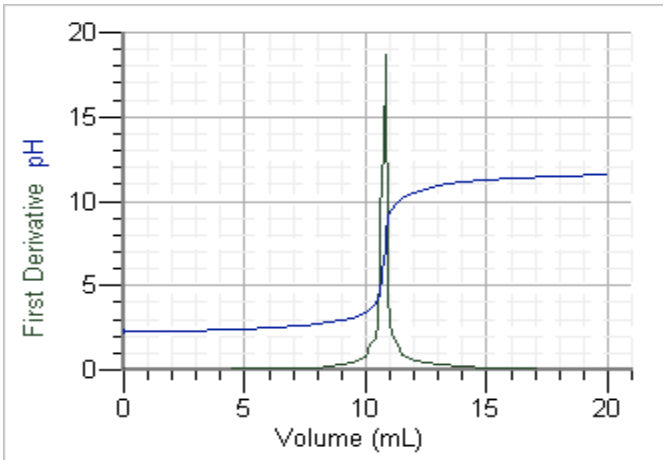
The most commonly used equipment for a titration is a manual buret in which the analyst (that's you!) opens and closes the stopcock, recording the pH after each addition of titrant. This is time-consuming and tedious. A more convenient method for recording a titration curve is to use an automated titrator that records both the volume of titrant added and the pH as a function of time. In this case the titrant is allowed to stream into the sample, usually at a slow rate, and the pH monitored continuously. In the Chem 260 lab this is accomplished using the LabPro software and the Vernier Drop Counter. Further details on their use is available on the course's web-site.

Processing Titration Data to Better Locate the Equivalence Point

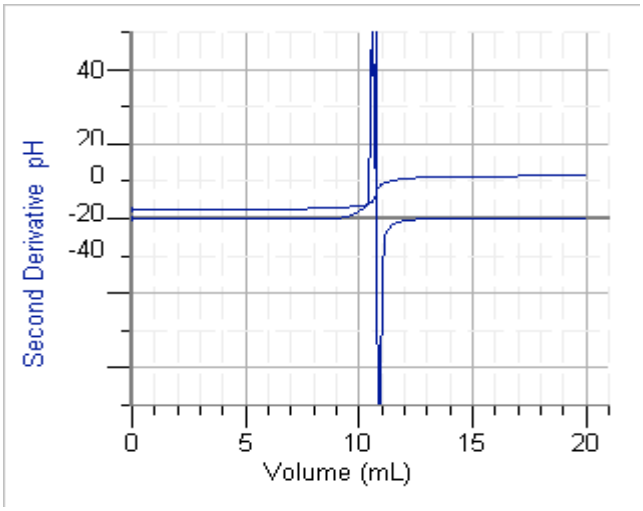
Generally, the limiting factor in using the data from a titration curve is the accuracy and precision of locating the equivalence point. Determining the equivalence point by a visual inspection of the titration curve, which is the most common method, can be tricky if the rate of change in pH near the equivalence point is not very large. Another approach, which sometimes overcomes this limitation, is to plot the titration curve's first-derivative; that is, to plot

$$\frac{d\text{pH}}{dV_{\text{titrant}}} \text{ vs. } V_{\text{titrant}}$$

This works because the first-derivative of a curve at any given point is the slope of the curve at that point. Because the equivalence point is where the rate of change in pH is greatest, the first-derivative will have its most positive (or most negative) value at the equivalence point. For example, when titrating an acid with a base, the titration curve and its first-derivative will look something like the figure shown on the right; note that the normal titration curve is shown for comparison.



Alternatively, one can plot the second-derivative, for the which the equivalence point is marked by the derivative's crossing of the volume axis (see figure below; again, the normal titration curve is shown for comparison).



One limitation to derivative techniques is that they enhance noise (random variations in pH not related to the addition of titrant) more dramatically than the analytical signal (the change in pH due to the addition of titrant). This can make derivative titration curves, particularly second-derivative titration curves, difficult to interpret.

Titrations Based on Other Types of Reactions

Although this tutorial uses acid/base reactions to explain titrimetry, any chemical reaction can serve as the basis of a titration provided that the reaction is favorable and occurs rapidly, and that there is a suitable means for determining the equivalence point. In this course we also use redox titrations, which are based on an oxidation/reduction reaction. The shape of a redox titration curve is similar to and acid/base titration curve, but plots oxidation/reduction potential vs. volume of titrant instead of pH vs. volume of titrant.

Potentiometry

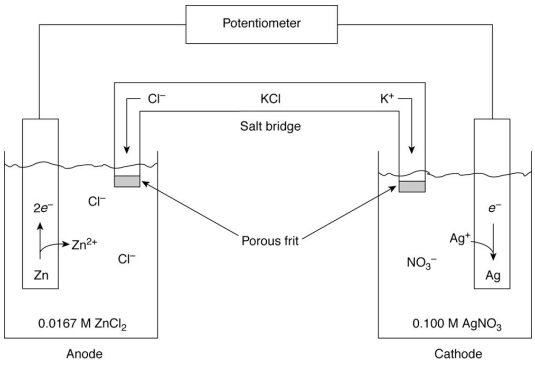
To obtain an acid/base titration curve similar to those shown in the previous section, it is necessary to monitor the sample's pH while adding the titrant. The most common way to measure pH is to use an electrochemical sensor that develops a measurable potential whose value is a function of pH. Such sensors are known as potentiometric electrodes and the technique is known as potentiometry.

The Basis of Potentiometry

In potentiometry we measure the electrochemical potential, E, of a redox system under conditions in which we do not allow the reaction to proceed (i.e. essentially no current flows); thus, the potential provides a measure of the reaction's thermodynamic favorability. Consider, for example, the reduction of Ag^+ by Zn

$$Zn(s) + 2Ag^+(aq) \leftrightarrows 2Ag(s) + Zn^{2+}$$

in which Zn undergoes a two election oxidation and the two Ag^+ ions each undergoes a one-electron reduction. As in any redox process, conservation of electrons requires that the electrons gained by the two Ag^+ions be provided by the electrons lost by the Zn. If we isolate the oxidation and reduction half-reactions in separate cells we can force the electrons produced by the oxidation of Zn to travel through a potentiometer where the potential can be measured (see figure to the right). This potential is given by the Nernst equation



$$E = E^o + \frac{RT}{nF}\ln Q = E^o + \frac{RT}{2F}\ln\frac{(0.0167)}{(0.100)^2}$$

where E^o is the standard state potential, R is the gas constant, T is the temperature, n is the number of electrons in the redox reaction, F is Faraday's constant and Q is the reaction quotient, which, in this case, is

$$Q = \frac{(Zn^{2+})}{(Ag^+)^2}$$

If E is positive, then ΔG is negative ($\Delta G = -nFE$) and the reaction is favorable as written.

Finding Concentration from Potential

When using a potentiometric electrode we usually are interested in determining the concentration of one ion in solution. For example, suppose that in the cell shown above the

concentration of Ag^+ is known to be 0.100 M, but that the concentration of Zn^+ is unknown. In this case the Nernst equation is

$$E = E^o + \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{(0.100)^2}$$

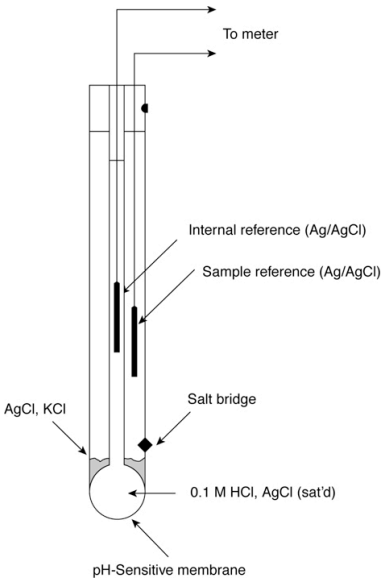
Measuring the potential allows us to calculate the concentration of Zn^{2+}. In principle the terms in the Nernst equation are well-defined and known; however, because of a variety of non-ideal behaviors, it is generally treated as having the following form

$$E = \hat{a}_o + \hat{a}_1 \ln \frac{[Zn^{2+}]}{(0.100)^2}$$

where β_o and β_1 are constants whose values, although constant, are unknown. To use the electrode, we measure the potential for two (or more) solutions containing known concentrations of Zn^{2+} and determine values for the two constants.

The pH Probe

A pH probe (see figure to the right) consists of a thin pH-sensitive membrane. This membrane is a specially manufactured glass that strongly binds H_3O^+. Because the concentration of H_3O^+ on the inner surface of the membrane (typically a solution of 0.1 M HCl) is different from that on the membrane's outer surface (the sample solution), the two sides of the membrane differ in charge and a potential develops. It is this potential that is related to the concentration of H_3O^+ in the sample. Before using the electrode it is calibrated using two buffers of known pH. One buffer generally is chosen to have a pH value near 7 and the other is more acidic or more basic depending upon whether the samples are acidic or basic.



Oxidation-Reduction Potential (ORP) Probe

Another common electrochemical sensor is the ORP probe. The probe's potential responds to all ions whose concentrations are determined by redox chemistry. When the potential is more positive, the solution is oxidizing and favors higher concentrations of more oxidized species. A more negative potential corresponds to a reducing solution that favors higher concentrations for more reduced species. ORP probes can be calibrated using solutions with known potentials, but more often they are used without calibration, providing relative information about the change in a solution's oxidizing or reducing power. An ORP probe, therefore, is useful for monitoring a titration that uses a redox reaction.

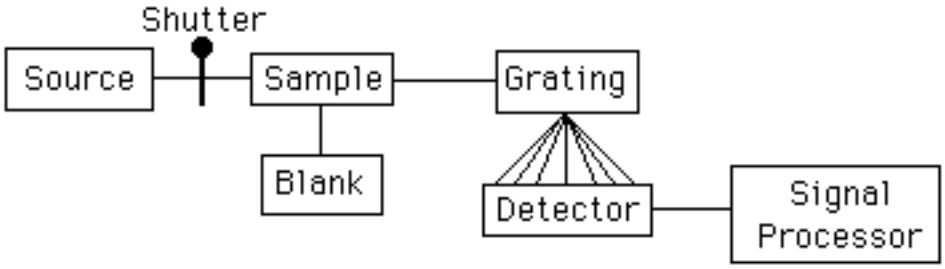
Visible Absorbance Spectra and Beer's Law

Why is orange juice orange? The simple answer is that one or more components of orange juice absorb selected wavelengths of visible light such that the light passing through or reflecting off the orange juice appears orange; that is, the sample absorbs light whose color is the complement of orange. We can take advantage of this phenomenon to study molecules, atoms, and ions by measuring their ability to absorb electromagnetic radiation. Sometimes this information is used qualitatively and other times it is used quantitatively.

Spectrometers

A sample's ability to absorb light is measured using a spectrometer. The simplest visible spectrometer consists of five parts: (a) a place to put the sample; (b) a source of visible light, typically a tungsten lamp similar to those you might find at home; (c) a detector for measuring the amount of radiation passing through the sample; (d) a means of dispersing the light, typically a prism or a diffraction grating, so that the light's interaction with the sample can be analyzed wavelength-by-wavelength; and (e) a signal processor, such as a meter or computer, for manipulating and displaying the resulting measurements.

In this course we will use the Ocean Optics USB2000, a simple cartoon of which is shown here.



This instrument uses a diffraction grating to disperse the light over 2048 individual detectors, each of which monitors absorbance over a narrow band of wavelengths.

Transmittance vs. Absorbance

At any wavelength, the fraction of light not absorbed by the sample is defined as its transmittance, T

$$T = \frac{P_T}{P_0}$$

where P_T is the intensity of light transmitted through the sample and P_0 is the intensity of light from the source. Frequently the transmittance is expressed as a percentage, %T, where

$$\%T = T \times 100$$

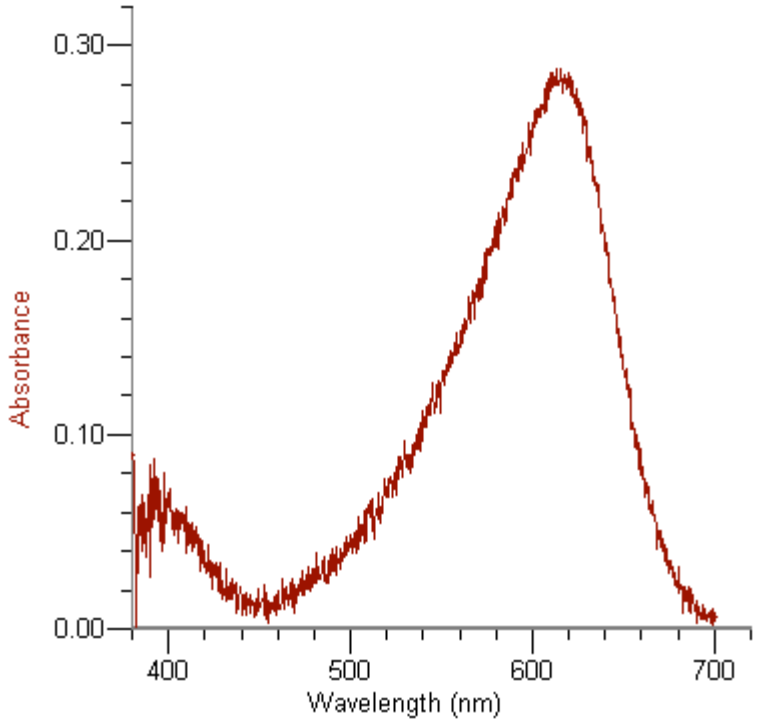
A little thought will convince you that transmittance must fall within the range of 0 to 1 and the percent transmittance must fall within the range of 0 to 100%.

For reasons that will soon be evident, the sample's interaction with light is more commonly expressed using absorbance, A, which is defined as

$$A = -\log(T) = 2 - \log(\%T)$$

Visible Absorbance Spectra

The Ocean Optics USB2000 spectrometer simultaneously monitors the absorbance (or transmittance) of light at 2048 different wavelengths. A plot of absorbance as a function of wavelength is called an absorbance spectrum, a typical example of which is shown below. Note that in this example the sample absorbs strongly at a wavelength of 618 nm.



Beer's Law

One of the most important applications of visible spectrometry is determining the concentration of the species absorbing light. As you might expect, solutions with a higher concentration of the absorbing species will transmit less light and will have a smaller %T.

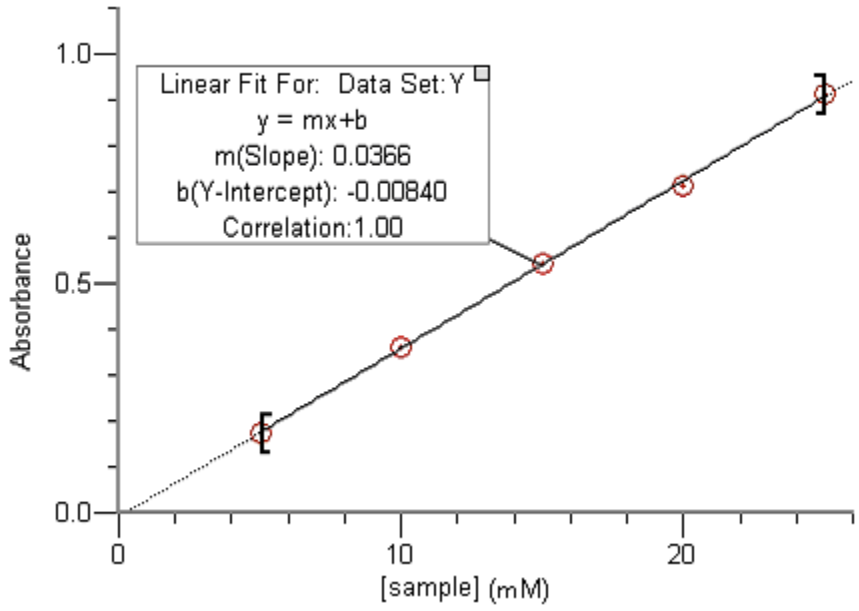
Unfortunately, the relationship between %T and concentration is logarithmic, which complicates the conversion of a sample's %T to the concentration of the absorbing species. The relationship between concentration and absorbance, however, is linear (this is why absorbance is ultimately more important than transmittance). The exact relationship between absorbance and concentration is known as Beer's law

$$A = \varepsilon bC$$

where A is the sample's absorbance, ε is a constant, called the molar absorptivity, whose value depends on the absorbing species and the selected wavelength, b is the distance the light travels through the sample and C is the molar concentration of the absorbing species. Values for ε are rarely known with sufficient accuracy, so they are determined by measuring the absorbance for a solution of known concentration. Usually we just combine the value for b with the value of ε and drop the stipulation that concentration must be expressed as molarity. Beer's law reduces, therefore, to

$$A = kC$$

where k is a calibration constant and C is any concentration unit. To determine the calibration constant we prepare several solutions containing known concentrations of the absorbing species, measure the absorbance of each and plot A vs. C. Linear regression is then used to find the best-straight line through the data (see the discussion of linear regression elsewhere in this manual). The equation of this line can then be used to calculate the concentration of the absorbing species given its absorbance. An example of a Beer's law calibration curve is shown here.



In this case the slope of 0.0366 is equivalent to k and the y-intercept, as expected, is essentially zero. Knowing the calibration equation allows us to calculate the concentration

of analyte in a sample. Thus, for example, if a sample gives an absorbance of 0.372, then the analyte's concentration is found as follows

$$A = -0.00840 + 0.0366C$$

$$0.372 = -0.00840 + 0.0366C$$

$$C = 10.4 \text{ mM}$$

Limitations to Beer's Law

Our treatment of Beer's law assumes that the relationship between absorbance and concentration is linear. This strictly is not true for a variety of reasons that we will not explore here; however, Beer's law closely approximates a linear relationship as long as the concentration of the absorbing species is sufficiently small and the absorbance is not too large. For this reason, it generally is a good idea to limited absorbances to values that are smaller than one.

Analyzing Data and Reporting Results

Although the work that you do in lab is important, it is but one step in the larger process of working as a scientist. Equally important are the planning that goes into identifying a research project and designing suitable experiments, and, after completing your work in lab, the analysis of your data and its presentation to others. Gathered here are some thoughts on the mathematical modeling of data, on the use of tables and figures as a means for organizing your data, and the preparation of a thorough and useful report. Topics covered include:

- Presenting Scientific Data and Results in Figures and Tables
- The Mathematical Modeling of Experimental Data
- Some Guidelines for Preparing a Formal Report

Presenting Scientific Data and Results in Figures and Tables

Suppose you are studying the growth of a magic beanstalk as function of time, recording data in your notebook, as shown below.

> August 28, 2004
> A bean from lot AG12, identified as AG12a, was planted at 10:05 AM and promptly watered and fertilized with a solution of Alice's Miracle Grow. The beanstalk's height was measured using a Jack and Son Model X15 laser-based tape measure, with the height taken as the distance between the ground and the point where the topmost leaf is attached to the beanstalk.
>
> 10:15 am: the beanstalk emerged from the ground
> 10:30 am: height is 9.96 m
> 10:45 am: height is 107 m
> 11:00 am: height is 329 m.
> 11:25 am: height is 763 m
> 12:05 pm: height is 1.21 km
> 12:35 pm: height is 1.32 km
> 1:00 pm: height is 1.34 km
> 2:00 pm: height is 1.34 km

In preparing a report of this study, how might you consider presenting your data? Obviously you wouldn't just transfer the writing in your notebook directly into your report; as written, the information is difficult for the reader to extract and understand.

Using Tables to Present Data. One way to present this data is in a table such as this.

Table 1. Height of beanstalk from bean AG12a at different times after planting.

Elapsed Time (min)	Height of Beanstalk (km)[a]
0	0
10	0
25	0.00966
40	0.107
55	0.329
80	0.763
120	1.21
150	1.32
175	1.34
235	1.34

[a] As measured from the ground to the point where the topmost leaf is attached to the beanstalk.

Note that the table is numbered and includes an informative title (positioned above the table), that each column begins with a descriptive entry and includes units (when appropriate), that the data in a column are aligned using the decimal points and that a footnote is included below the table to supply information not included in the report's text. Note, as well, that the less useful measurement of absolute real time has been converted into an elapsed time and that the heights have been converted to a common unit. This table contains all the information recorded in the lab notebook in a format that makes it easy for the reader to see the relationship between time and the height of the beanstalk.

Although not appropriate for the data in Table 1, it often is useful to include a statistical summary of your data. Table 2, for example, reports the maximum height of bean stalks grown from beans taken from the same lot, along with the mean and standard deviation.

Sample ID[a]	Maximum Height (km)
AG12a	1.34
AG12b	1.24
AG12c	1.48
AG12d	1.38
AG12f	1.31
mean	1.35
std dev	8.89×10^{-2}

[a] Sample AG12e did not germinate and is not included in this summary.

Using Figures to Present Data. Another way to present the data in Table 1 is as a figure showing height as a function of elapsed time (see below). Note that the figure is numbered and includes an informative title (positioned below the table), that the data points are clearly marked with point protectors (○), that the scales for the axes spread the data over the figure's available space and that the axes are labeled with descriptive titles (including units where appropriate). One advantage of using a figure is that it allows you to highlight your analysis of the data. For example, this figure shows results of modeling the data using the following equation

$$\text{Height} = A \times e^{-(\text{Elapsed Time}-B)^2/c^2} + D$$

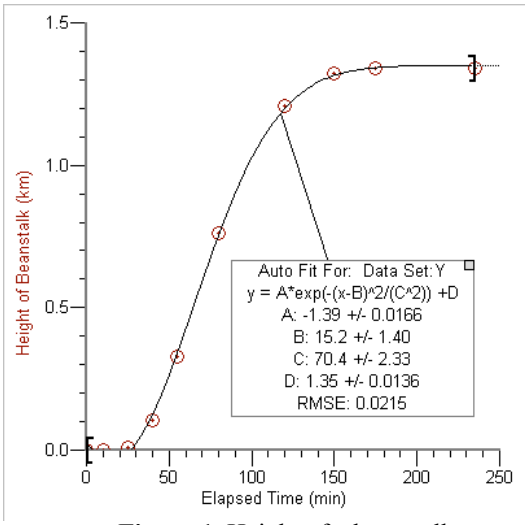


Figure 1. Height of a beanstalk from bean AG12a as a function of time after planting.

Figures also can be used to display several related sets of data. For example, the figure on the next page shows results for three trials. Note that the figure includes a legend to help identify each set of data. This figure also connects the points with line segments to further highlight the relative trends in the data sets. Note, as well, that this figure includes a grid to aid in reading the graph. Connecting points with line segments and including grid lines are not common choices but they can be effective in some situations; use them judiciously.

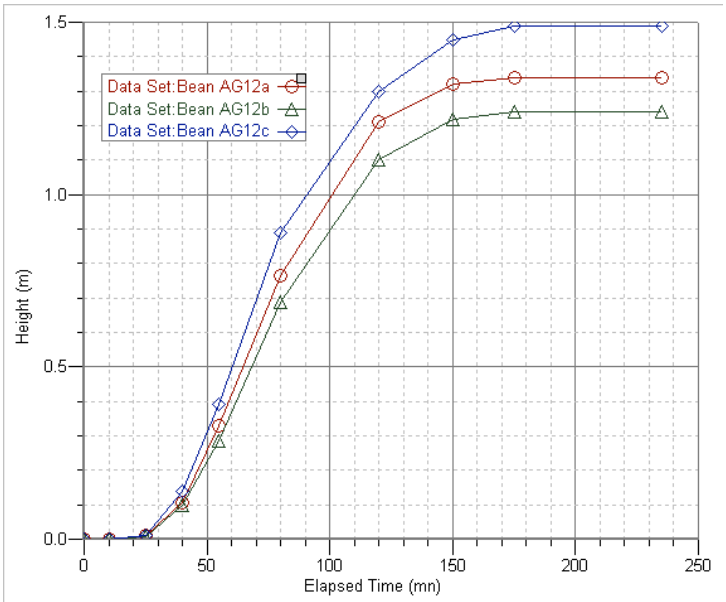


Figure 2. Heights of beanstalks grown from three beans selected at random from lot AG12 as a function of time after planting

Figures 1 and 2 are examples of good figures. In Figure 1, for example, the actual data are clearly identified, providing a means for visually evaluating how well the equation fits the data. In both figures the data occupy the available space, allowing for a visual appreciation for the data's trend. For example, in Figure 2 we can see that all three growth curves are sigmoidal in shape with a similar lag time between planting and emergence of the bean stalk. We also can clearly see that there is some variation between the three beans with respect to their growth rate and the maximum height of the mature plant.

A poorly prepared figure hides important information. Consider, for example, Figure 3, which shows the temperature for a sample of porridge as it cools. Including the thermometer's full scale on the y-axis (0°C to 240°C) has the effect of compressing the data to a small portion of the available space, making the nature of the cooling more difficult to see. Furthermore, the absence of point protectors obscures the data. Finally, the caption does not suggest why the first part of the data was not included when modeling the data.

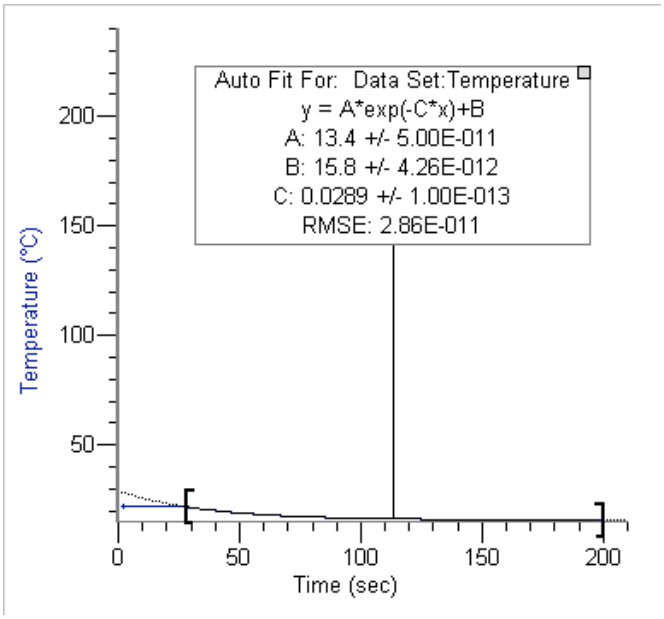


Figure 3. Cooling curve for Baby Bear's porridge.

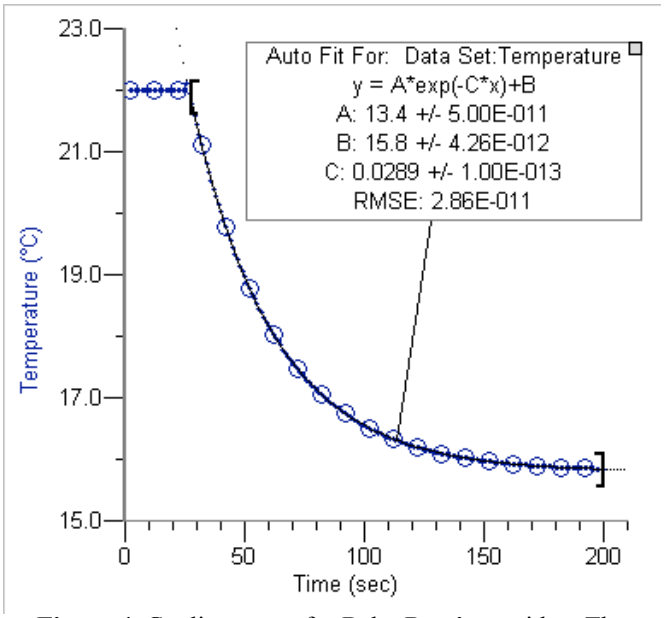
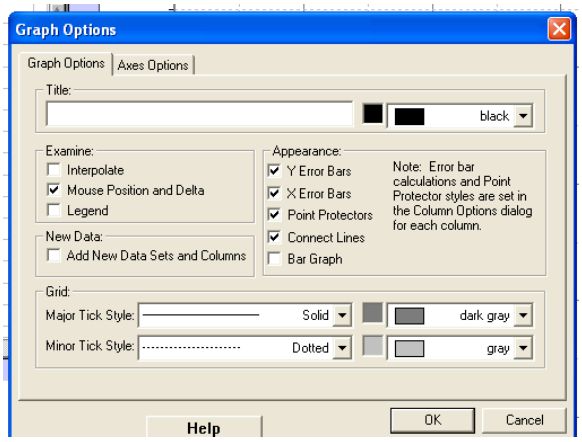


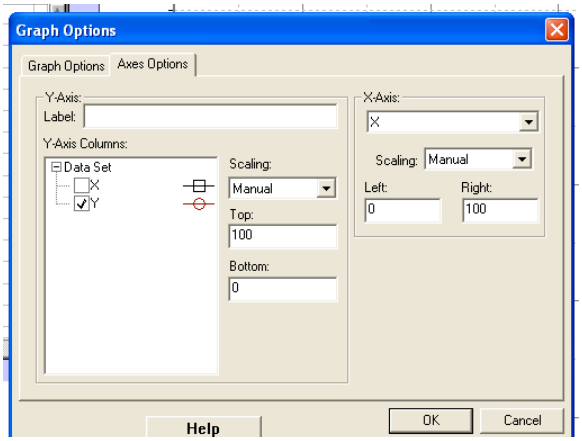
Figure 4. Cooling curve for Baby Bear's porridge. The sample was removed from the stove at t = 25 sec.

A better figure is shown on the left. Note that in this figure the scale on the y-axis spans only the relevant temperatures, making it easier to see the cooling curve. The use of point protectors makes the data easier to see and improves our ability to evaluate the quality of the fit between the data and the theoretical equation. Note, as well, that the figure's caption clarifies why the first 25 seconds of data were not included when modeling the data. This figure is one that provides the reader with a useful summary of the data.

Preparing Figures Using LoggerPro or Graphical Analysis. Much of the data you will collect in lab this semester will be through the LoggerPro interface. Because this program has very good tools for displaying data, you will find that it is an excellent way to prepare figures. Graphical Analysis, which is simply a version of LoggerPro without data collecting abilities, is also an excellent tool for preparing figures. The remainder of this section provides some useful information about altering the appearance of your figures.

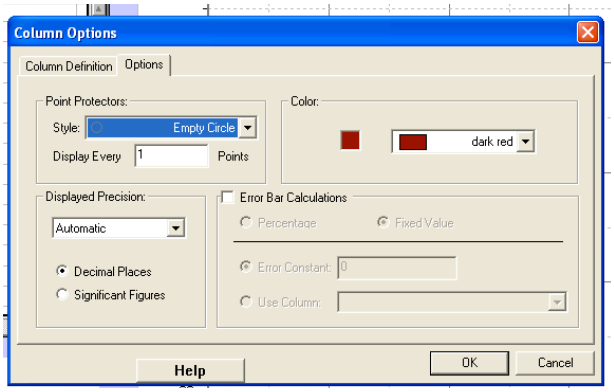
To modify the program's default choices for displaying data, click on the figure and select Options: Graph Options… from the main menu. This brings up the Graph Options window, which has two tabs for altering the appearance of the data and the axes. On the Graph Options tab (shown on the right) you can choose to display point protectors, to connect individual data points with straight line segments and to add a legend to your figure. You also can add a title and change the style of major and minor gridlines (including the choice to omit gridlines).





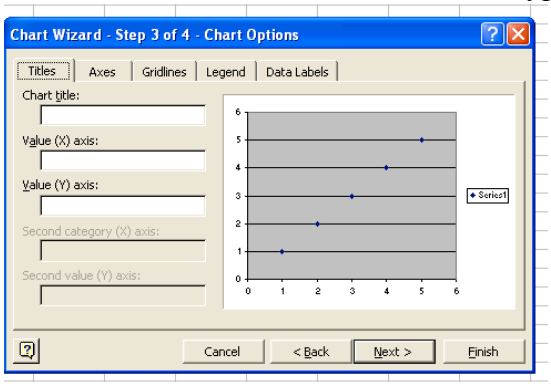
From the Axes Options tab (shown on the left) you can choose which data set to plot on the x-axis and which set(s) of data to plot on the y-axis. You also can adjust the scale of the axes using the option for man-

ual scaling. To replace the default title for the y-axis, enter the desired title in the box for the y-axis label. To change the title for the x-axis you must change the data set's title. Click on the data table and select Data:Column Options and the x-axis data. On the column definition tab enter the title you wish to display on the x-axis.



Further manipulations of the figure are accomplished using the Column Options. Click on the data table and select Data:Column Options and the y-axis data you wish to modify. Select the Options tab (shown to the right). Here you can choose the symbol for the point protectors and how frequently they are displayed. Although all data points are shown on the figure, it often is best to highlight only a limited number of points with protectors to improve visibility and readability. You can also change the color used to display the data set.

Preparing Figures Using Excel. Although you are encouraged to use Graphical Analysis to prepare figures, you may, at times, wish to use Excel instead. To use the directions given here your data must be organized such that the left-most column contains the x-axis data with the remaining columns containing one or more sets of data to be plotted on the y-axis. Click and drag over the data and select Insert:Chart… from the main menu, which launches the Chart Wizard. Select the type of chart that you wish to create (an xy-scatter plot is almost always the correct choice) and the desired chart sub-type (normally a plot displaying the data points without lines). Proceed to the Chart Wizard's third screen (shown to the left) where you can enter a title for your figure and labels for the x-axis and y-axis, select which gridlines to include and add a legend. When your figure is complete you can make changes by clicking on the figure and double-clicking on the feature you wish to change. For example, Excel defaults to a background color of gray for the figure. To remove this color, which is a good idea, double-click on the background (what Excel calls the plot area) and select none.



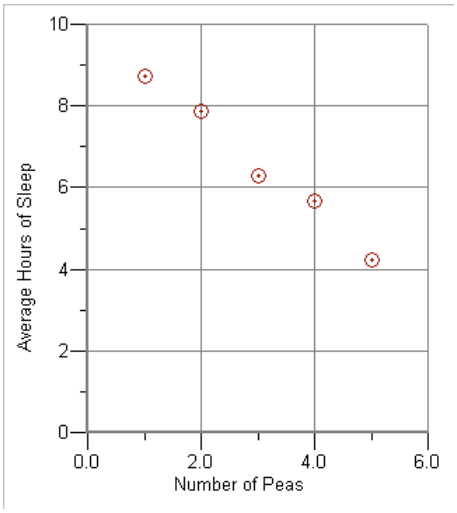
When to Use Tables and When to Use Figures. So, which is the best method for presenting data – a table or a figure? If your emphasis with a particular set of data is to show a trend or to demonstrate that a theoretical model explains your data, then a figure is usually the best choice. On the other hand, when exact numerical values or a statistical summary are important, then a table is the better choice. In general, for any data set, you should use a figure or a table, but not both.

The Mathematical Modeling of Experimental Data

In an experiment we usually measure a response for one or more variables as a function of a variable whose value is directly under our control. In the language of experimental design, the variable under our control is the independent variable and the variables whose values we measure are dependent variables. For example, consider the following hypothetical data for an experiment designed to determine the effect on a Princess's sleep of placing peas under her mattress.

Number of Peas Under Mattress	Average Hours of Sleep Obtained by Princess
1	8.72
2	7.86
3	6.29
4	5.68
5	4.22

In this experiment the number of peas placed under the mattress is the independent variable; that is, this is the variable under our control. The average hours of sleep, therefore, is the dependent variable. A graph of this data (see below) shows what appears to be a inverse linear relationship between then number of peas placed under the mattress and the average hours of sleep. Seeing this relationship we might ask questions such as "What is the relationship between the average hours of sleep and the number of peas placed under a mattress?" or "If we place seven peas under the mattress, how many hours might the Princess sleep?"



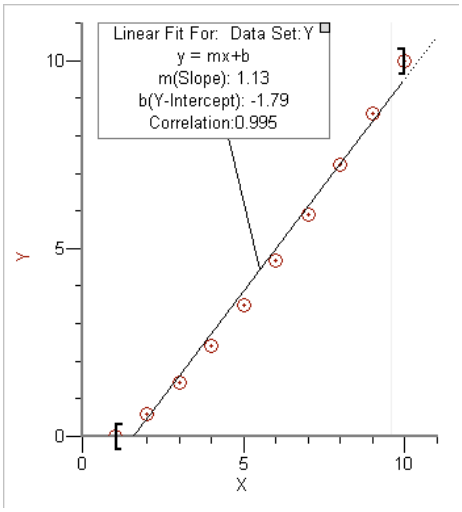
Regression Analysis. To answer questions such as those suggested above requires a suitable mathematical equation that appropriately models the data. This is the realm of a regression analysis. For a straight-line relationship the model equation is

$$Y = \beta_0 + \beta_1 X$$

where Y (the dependent variable) is the average hours of sleep, X (the independent variable) is the number of peas placed under the mattress, β_0 is the average hours of sleep obtained in the absence of any peas (the value of Y when X is zero, or the y-intercept) and β_1 is the average number of hours of sleep lost per pea (which is also the slope of the line or the rate of change of Y relative to X; that is, $\Delta Y/\Delta X$). The terms β_0 and β_1 are consider adjustable fitting parameters of the model. The goal of a regression analysis is to find the best values for β_0 and β_1 such that the net difference between the experimental

values of Y and those values predicted by the model is as small as possible.[1] The mathematical details of how this is accomplished are too involved for this course. Fortunately, we have access to software packages that can carry out the analysis for us.

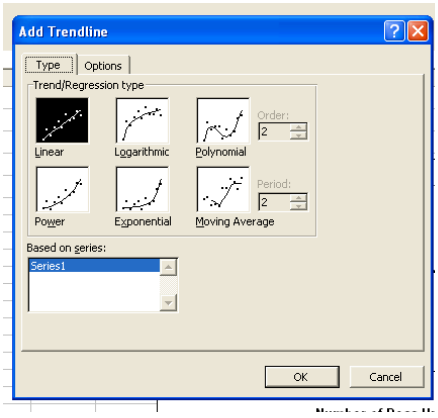
Of course you can fit a straight-line to any set of data, even if the data clearly are not linear. For this reason it is important to examine the results of a regression analysis and determine whether your model is reasonable. One common way to evaluate what is often called the model's "goodness of fit" is to look at the correlation coefficient, R, or the coefficient of determination, R^2, which are two measures of the degree to which the model explains the data. A value of R close to +1 or -1 (or an R^2 close to +1) suggests that the model does a good job of explaining the data and a value close to 0 suggests that the model is inappropriate.



Unfortunately, the correlation coefficient and coefficient of determination are not always a very sensitive measure of a model's suitability. Large values for R or R^2 can falsely lead you to assume that the model's equation provides an accurate description of the data. A much better choice is to graph both the data and the predicted model's curve and examine them critically. If a model is appropriate then you should see that the model closely fits the data with individual data points randomly scattered around the model's predicted curve. Note that although the example shown on the left has a very favorable value for R^2, the data clearly show evidence of curvature with values of Y at low and high values of X found above the model's curve and values of Y for intermediate values of X falling below the model's curve. A quadratic model of the form

$$Y = \beta_0 + \beta_1 X + \beta_2 X^2$$

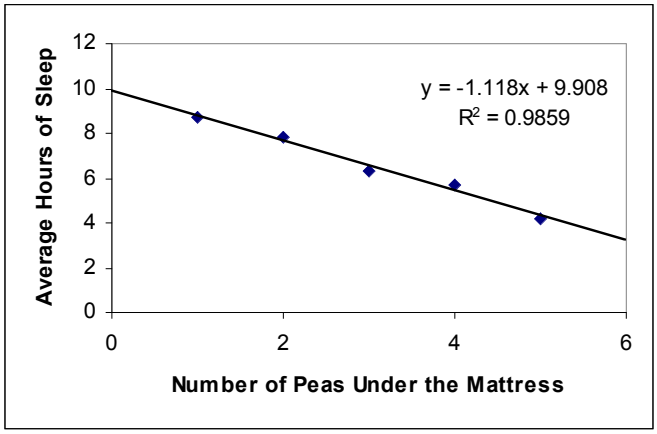
is probably a better choice for this data.



Using Excel for a Regression Analysis. You may already be familiar with using Excel to complete a regression analysis and know how to add the resulting model's curve to a chart. If not, then here are a few instructions. Begin by creating your chart using the data provided above. Click on the chart and select Chart:Add Trendline… Note that there are six options, one of which is for a linear trend. Select the op-

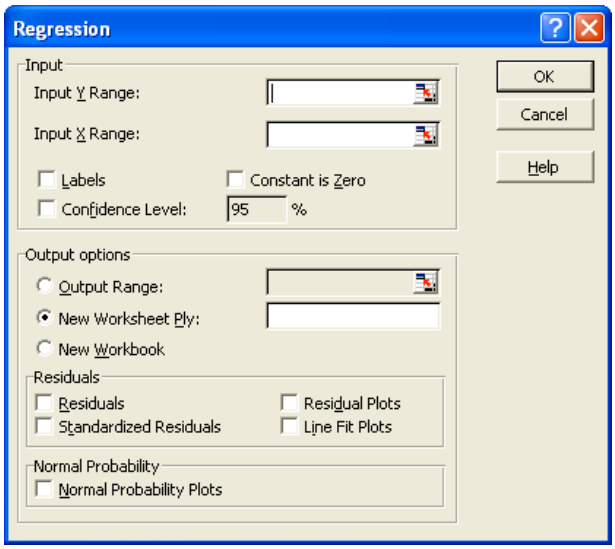
[1] You may be more familiar with expressing a straight-line in the form $Y = mX + b$, where m is the slope and b is the y-intercept. The use of β_0 and β_1, however, is the more standard statistical form of the equation.

tions tab and click on the appropriate boxes to add the equation to your chart and to display the R^2 value. By default, Excel only displays the regression line from the first value to the last value on the x-axis. If you wish to extend the line in either direction you can do so using the forecast section of this window and indicating how many units on the x-axis to extend the line. When complete your chart should look similar to that shown below. Note that this example extends the model one unit in either direction along the x-axis; that is to values of X corresponding to zero and six peas.



Using Excel to complete a regression analysis is not without its limitations. As shown above, Excel has a somewhat limited choice of mathematical models and does not allow you to specify other models. Furthermore, in some cases the equation provided by Excel includes too few significant figures for β_0 and β_1 to be of practical use. To increase the number of significant figures, click on the equation and select Format:Selected Data Labels… Chose the option for Number and specify the appropriate format.

Excel has a more powerful regression tool that overcomes the limitations of the trendline tool. To access this tool, select Tools:Data Analysis… from the menu bar. From the list of available data analysis tools, select "Regression" and click on the button labeled OK, which gives the window shown to the right. Place the cursor in the box labeled "Input Y Range" and then click and drag over the appropriate data in your spreadsheet. Place the cursor in the box labeled "Input X Range" and then click and drag over the appropriate data in your spreadsheet. Check the box for "Labels" if your input ranges for X and Y include labels. Click the button labeled "Output Range" and then place the cursor in the adjacent box. Click the cell in your spreadsheet that is to be the upper-left cell for the regression summary, or select the button labeled "New Worksheet Ply" if you want the summary to appear in a new worksheet. The resulting output, which is shown on the next page, contains lots of information; for our purposes the most important details are the intercept and slope, which are the coefficients in the third table. Note that the slope is identified using the label for the y-axis data.



SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99291243
R Square	0.9858751
Adjusted R Square	0.9811668
Standard Error	0.24432219
Observations	5

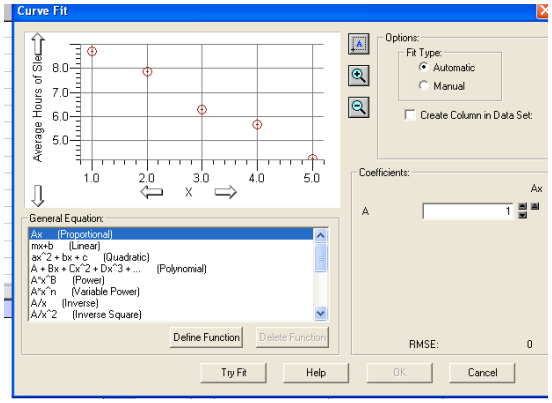
ANOVA

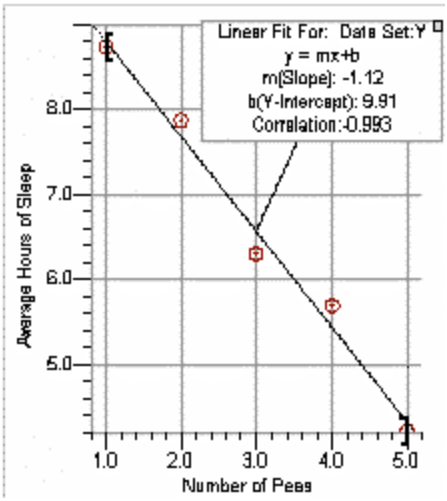
	df	SS	MS	F	Significance F
Regression	1	12.49924	12.49924	209.3909	0.000715513
Residual	3	0.17908	0.059693		
Total	4	12.67832			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	9.908	0.256247276	38.66578	3.81E-05	9.092506037	10.72349396	9.092506037	10.72349396
Number of Peas Under Mattress	-1.118	0.077261461	-14.47035	0.000716	-1.363880681	-0.87211932	-1.363880681	-0.872119319

You can use this approach to fit more complicated models; see your instructor for details.

Using Graphical Analysis or Logger Pro for a Regression Analysis. Graphical Analysis (or LoggerPro) provides a better choice for completing a regression analysis. Here are some instructions. Begin by creating a graph of the data provided above. Select Analyze:Curve Fit… from the main menu, providing the Curve Fit window shown to the right. The scrolling menu at the bottom of the window provides a range of functions. Select the appropriate function and click on the Try Fit button to preview the result. If acceptable, click on OK to accept the result. You should obtain a result similar to that shown to the left. Note that for a straight-line model Graphical Analysis provide the correlation coefficient (R) instead of the coefficient of determination (R^2). For other models, Graphical Analysis reports the root mean square error (RMSE), which is defined as



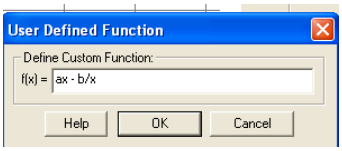


$$\text{RMSE} = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{n}}$$

where y_i is an experimentally determined value the i^{th} value of x, $\hat{y}_i$ is the model's predicted value for y_i, and n is the number of measurements. The smaller the RMSE, the better the fit between the model and the data.

Graphical Analysis provides two important features that are not available with Excel's trendline function. First, by clicking and dragging the brackets on your graph (the **[** and **]** in the figure above) you can alter the portion of your data included in the regression

analysis; the model's predicted equation adjusts automatically. Second, you can use the Define Function button on the Curve Fit window (see earlier figure) to include a model that is not included with the software. Shown to the right, for example, is the format for entering the model



$$Y = aX - b/X$$

where *a* and *b* are coefficients whose values are determined by seeking to minimize the net difference between the experimental values of Y and those values predicted by the model.

Interpolating and Extrapolating From a Model. To create a mathematical model for a system you measure the dependent variable for several known values of the independent variable. The reason for developing the model, of course, is to predict the value of the independent variable (or the dependent variable) for samples where its value is unknown. For example, we have shown that a Princess's average hours of sleep is a function of the number of peas placed under her mattress.

$$\text{Avg. Hours Sleep} = -1.118 \times \text{Number of peas} + 9.908$$

We can use this model in two ways. If we know how many peas we plan to place under her mattress, we can predict how long she will sleep. Alternatively, if we measure the number of hours that the Princess sleeps on a given night, we can predict how many peas are under her mattress. These are powerful and useful applications of a model; however, when using a model to make predictions we need to be careful when interpreting the results. Here we need to make an important distinction between interpolation and extrapolation.

In developing our model we used 1 – 5 peas. Based on our analysis of this data, we have every confidence that the mathematical model works well for this range of peas and the associated range of average hours of sleep. If we limit the model to making a prediction within this range, a process called interpolation, our confidence in the prediction's accuracy is high. For example, if we determine that the Princess slept 6.0 hours, we can predict that there are 3.5 peas under the mattress and be confident in this prediction.

Extending the model to values of the dependent variable and independent variable that we did not study, a process called extrapolation, is possible but more susceptible to uncertainty. If the Princess sleeps 9 hours our mathematical model suggests that there probably were no peas placed under her mattress. This extrapolation of our model to smaller values of the independent variable seems reasonable as there is no reason to believe that the linear behavior between 1 and 5 peas does not hold between 0 and 1 peas.

Can we safely extrapolate the model to larger values of the independent variable? What is our prediction, for example, if we place 10 peas under the Princess's mattress. Using our model, we predict that the Princess will sleep for –1.272 hours, a result that is impossible.

We clearly cannot extrapolate our model this far. Given this contradiction, it is tempting to modify our model by assuming that it is valid until the dependent variable reaches zero. Such an assumption, however, is still fraught with potential uncertainty. Suppose the Princess sleeps for 2.0 hours. Extrapolating our model leads us to predict that there are 7 peas under the mattress; however, it also is possible that the Princess will sleep a minimum of two hours regardless of the number of peas under the mattress. If true, then we cannot extrapolate the model to 2.0 hours or less of sleep.

When building models for a system it is important to consider how you plan to use the model and, if possible and practicable, to ensure that the range of values for the independent variable spans the range of values you wish to model. In this way your predictions rely on interpolations and not extrapolations. If an extrapolation is necessary, be sure to consider its limitations.

Some Guidelines For Preparing a Formal Report

The results of laboratory work generally are shared with other scientists in articles written for scientific journals. Although scientists often present oral or poster papers at professional meetings, such work is usually preliminary and tentative. When research reaches the point where a convincing story can be told, then publication in a suitable journal is the appropriate way to let others know of your results.

If you look at a variety of scientific journals you will find that there are many formats for research articles. Each journal, however, remains true to its format, most of which include the following items: a title, an abstract, an introduction, the procedure, the results and conclusions, references and notes, and appendices.

Although these items usually are a part of any research article, some journals combine them in different ways. For example, it is not unusual for the results and conclusions to be in separate sections.

For the purposes of this course we will use the format listed above for formal reports. The remainder of this document provides some suggestions for each section of a lab report.[1] You might find it useful to refer to the sample report in Appendix One as you read through the following description of reports. *Note – Your electronic notebook and a formal report have different purposes. In general, copying and pasting the contents of your notebook into your report is a poor idea.*

Writing the Title. A good title should be brief (15 words or less) and clearly identify the problem you investigated or a description of your results. Don't use the experiment's title as the title for your report.

Writing an Informative Abstract. A good abstract provides a brief (3-6 sentence) descriptive summary of your report's major points. At a minimum it should clearly state the goal(s) of your work, the key technique(s) used and a summary of your key result(s), including the expected result(s) when known. Because the abstract summarizes your work, you should prepare it after writing the remainder of the report. For a formal report the abstract is the first thing I read, providing me with a sense of where to focus my attention. For example, if your results are clearly in error then I will give extra attention to your data, calculations and experimental design. Or, if your description of the experiment's purpose is confusing then your understanding of the experiment may be weak; in this case I will give extra attention to your introduction.

Writing a Thorough Introduction. The introduction to your laboratory report should accomplish three things: it should clearly explain how your experiment fits within the broader context of the course's three main topics (i.e. thermodynamics, equilibria, and kinetics), it should explain why your experimental approach is suitable and briefly outline

[1] There are many good sources of information about technical writing. The suggestions compiled here were culled from Porush, D. *A Short Guide to Writing About Science*, Harper and Collins: New York, 1995.

any relevant theory, and it should clearly state the goal(s) of your experiment. Many of these issues are, of course, outlined in the experiment's handout and you may use this as a starting point when drafting your introduction. A good introduction, however, will not just repeat information from the experiment's handout, but will extend and contextualize it. Use the introduction to define terms, explain basic theory and to convince me that you understand the experiment's goals. *Searching for additional information in the library or on the internet is appropriate and desirable.*

Writing a Useful Procedure. This is often the hardest part of a report to write well. Surprisingly, your initial effort will inevitably provide too much detail instead of too little detail! Here are some useful guidelines to consider:

- A procedure <u>is not</u> a list of what you did in lab; it <u>is</u>, however, a well-written narrative. Avoid using phrases such as "First we…" or "Next we…".

- A procedure <u>does not</u> describe the specific things you did in lab; it <u>does</u>, however, provide a general guideline to what you did. For example, you don't need to state that "We evaluated the cooling rate of porridge using initial temperatures of 60 ^{o}C, 55 ^{o}C, 50 ^{o}C, and 45 ^{o}C," because you will include these temperatures as data in your results and conclusions section. You should state, however, that "The porridge samples used to evaluate cooling rates were heated using a gas stove while stirring with a wooden spoon." Or, you don't need to mention that "We prepared a dilute solution of 2.00×10^{-3} M hemlock by adding 5.00 mL of a 0.100 M stock solution to a 250-mL volumetric flask and diluting to volume with spring water." What is important is the concentration of your final hemlock solution, not its volume. It is more appropriate to write that "A solution of 2.00×10^{-3} M hemlock was prepared from the available 0.100 M stock solution."

- A procedure <u>does</u> provide information on the reagents used in the experiment. Be sure to list all reagents provided for your use or prepared by you (e.g. "Solutions of 6.00 M hemlock and reagent-grade powdered toadstools were used as supplied." or "A solution of 0.10 M hemlock was prepared using the provided 6.00 M stock solution and a 5.0 % w/v solution of toadstools was prepared using reagent-grade powdered toadstools.").

- A procedure <u>does</u> provide information on the major equipment used during the experiment. Be sure to identify the make and model of all instrumentation, computer hardware and software. Where specific operating conditions are used, be sure to specify them (e.g. "Cooling curves for porridge samples were measured using a CelFar thermometer interfaced to a Merlin Microcomputer equipped with a NEWTon data interface. Temperature measurements were made every five seconds until the porridge's temperature reached 30 ^{o}C.").

- A procedure <u>might</u> mention the type of glassware and minor equipment used in the experiment but only if the choice is crucial or unusual. For example, if it es-

sential to collect samples of witch's brew using gold-lined sampling bottles, then say so. In general, there is no need to specify the type of glassware as this made evident by the proper use of significant figures. If your procedure states that a nominally 0.1 M solution of hemlock was prepared, then it is clear that volume measurements were approximate (e.g. a graduated cylinder and a bottle or beaker). On the other hand, if your procedure states that a 0.100 M solution of hemlock was prepared, then it is clear that volumetric glassware was used.

- If your procedure closely follows a previously published procedure, then you may simply make a reference to it and note any significant modifications. Thus, you might write that "The number of plums in a pie was determined using the method of Horner (*13)* with the modification that individual plums were removed using a fork instead of the thumb."

Presenting Your Results and Conclusions. This is the heart of your report so it deserves your greatest attention. The most important requirement of this section is that it must be a well-written narrative that clearly guides the reader through a presentation of your data and your analysis of that data. Use tables and figures to organize your data and to enhance its presentation. Be sure that you refer in your narrative to each table and figure and guide the reader to see the specific point(s) of information contained within. Remember that your goal is to make a convincing argument about the analysis of your data and to arrive at specific conclusions that are well-supported by your data. Don't leave this to the reader! Finally, be sure to evaluate the reasonableness of your results. If you know the expected results for the experiment, then compare your conclusions to them and discuss possible sources of error. When discussing sources of error do not cite "human error;" you may assume that you correctly used your equipment. Instead, consider other sources of errors that might reasonably account for the magnitude and direction of you error.

Referencing Other Works. Every discipline has its rules for preparing references. In most chemistry journals references are cited in the text using italicized numbers listed within parentheses (e.g. (*1*)) or as superscripts. References may be placed either at the bottom of the page where the reference is made or collected, in numerical order, at the end of the report. Use the following standard formats:

- Journal articles: Green, A.; Scarlet, R., "Preliminary Measurements on the Strength of Huts Made Using Bricks: Can They Withstand the Huffs and Puffs of Wolves?" *Folk Tales Sci.*, **2003**, *45*, 313-315.

- Books: Blue, V. *A Brief History of Magic Potions*, Merlin Press: Salem, MA, 1999.

- Chapter or article in book with editor: White, B., "Seeking a New Means for Spinning Straw into Gold" in *Studies in Alchemy*, Black, C., ed., Merlin Press: Salem, MA, 2001.

- Internet sites: http://www.goldilocks.com/mattresshardness/ (accessed January 2008)

Making Using of Notes. There are two important aspects of your report—derivations and calculations—that frequently should be included, but whose presence detracts from a smoothly written narrative. One way to include this material without distracting the reader is to place it in a note appended to the back of the report. For example, you might write the following: "Assuming that breaking a standard hand mirror causes seven years of bad luck, we know that Sleeping Beauty's step-mother can expect an additional 23.6 yrs of bad luck (Note 1)." In the note you can then work through the relevant calculation.

Appendices. Inevitably you will gather more data than you need to include in your report. Use this section to list additional tables and/or figures that support your work and that you wish me to examine (as needed). The tables and figures should be gathered together in a folder labeled "Appendix" and placed within the experiment's folder included within your group's I-drive folder. Include in your lab report a brief outline of what supporting information is in the appendix.

Verifying Your Work. Most of the time your results will be reasonable; that is, the data you collect and the results you report are within expectations even if they have more uncertainty than might be desirable. When your results are at odds with expectations, however, it may be because of lousy data or good data that are incorrectly analyzed. Between your results and conclusions section, your notes and any supporting information in your appendix, it must be possible for me to reconstruct your work. If I can't, then several areas of your report are likely to be judged unacceptable.

Stylistic Considerations for Scientific Writing. Finally, grammar, spelling and formatting matter, as does well-written prose. *The quality of your writing in this course should be no different than that for courses in the humanities or social sciences*. A few specific suggestions are provided here:

- Be concise. Use simple words. Write short sentences. Thermodynamics, equilibria, and kinetics are tough enough to understand; there is no need to make them more complicated by writing confusing, wordy sentences.

- Remember the basic structure for writing a good essay. Introduce a paragraph's main idea with a topic sentence and develop the idea throughout the remainder of the paragraph. Link your paragraphs together with smooth transitions.

- Words have specific meanings. This is particularly important in scientific or technical writing. Rate and energy, for example, have many definitions, but in the context of this course their meanings are very specific. Be sure that you use them correctly.

- Numbers have significant figures and units. You know this, so use them properly. In scientific writing the use of significant figures carries meaning. When you say

that "A 0.127 g portion of dried toadstools was reacted with…," listing three significant figures tells the reader that the mass was weighed on a balance with three decimal places. If the same statement simply said "0.1 g of dried toadstools" the reader would rightly assume that the experimenter simply used an approximate means of measuring the sample, such as the amount fitting on the tip of a spatula. While on the subject of numbers, a decimal point is placed between numbers; the decimal equivalent of ½ is 0.5. Writing 0.5 as .5 can be confusing to the reader, who may not notice the decimal point and believe that the value is 5. Finally, if you must begin a sentence with a number, write out the number; thus don't write "5-L of hemlock were obtained"; instead, write "Five liters of hemlock were obtained."

- Use captions, legends, and footnotes to explain the contents of figures and tables. Even though you will discuss a figure or table in your narrative, a caption helps focus the reader's attention. Figures containing more than a single set of data should include a legend, either incorporated into the caption or imbedded in the figure, identifying the data sets. Make use of footnotes in tables to add helpful annotations.

- Sequentially number equations included in your narrative. The appropriate format is to center the equation on its own line (rather than including the equation in the middle of a line of text) and place the numerical label in brackets at the right margin; thus

$$PV = nRT \qquad [1]$$

  Rather than retyping the equation later, you can simply refer to it by its number. For example, "Rewriting equation [1] as…"

I'm Suffering From Writer's Block! How Do I Get Started? Writing a formal lab report can be a daunting task. Here is a suggestion of how to get started. Begin by thoroughly organizing and analyzing your data. As you do this you will created many tables and figures; cull through these and select those that most efficiently summarize your data and results and that are most crucial to your conclusions. Next, write the narrative for the results and conclusions section, building it around your tables and figures. Write the procedure section after you complete the results and conclusions section. As you write your procedure, focus on ensuring that a similarly experienced peer could explain how the data presented in the results section were obtained. Finally, write your abstract at the very end.

But what about the introduction? You can write this at any point as it is independent of your procedure, data and results (although it does define the problem on which you were working). You might even (gasp!) want to begin working on your introduction as you begin preparing for the lab.

How Does a Group Write a Report? Your reports are group effort. It is worth considering, therefore, how a group might work together to produce a quality report. One ap-

proach is to assign one group member the task of preparing an initial draft on which the remaining group members can comment. This first draft is then rewritten and reviewed again (and again, as needed). This is the approach we will use with the reports for the preliminary experiments.

A second approach is to divide the report into three or more parts, with each member taking responsibility for one or more parts. An obvious way to divide the report is into the introduction, the procedure, and the results and conclusions. The advantage to this approach is that the workload is more equitable. This approach, however, often leads to reports that read poorly due to differences in writing styles, that become repetitive because information is repeated in three places or that omit important information because each group member thinks that the others will include it when writing their sections. This is the approach we will use with the report for the final project lab.

Regardless of the approach your group decides to use, the three most important thing you can do to ensure a well-written and thorough group report are:

- *Don't procrastinate!* Get an early start on your writing so that you have ample time to conduct any necessary research, to completely analyze your data and to give others a chance to read through and comment upon your work. Agree on intermediate deadlines and keep to them.

- *Write multiple drafts!* Prepare an initial draft for yourself and edit it before preparing a second draft to share with your group. Incorporate their comments into a third draft, which should then need only minor corrections before preparing the final report.

- *Remember that your report is a collaborative effort!* Don't become so enamored of your prose or your ideas that you find it difficult to listen to the ideas of other group members. Share ideas with each other and maintain an open mind.

Preliminary Experiments

The purpose of the first four experiments, each of which takes a single lab period, is to provide you with an opportunity to:

- become familiar with the electronic laboratory notebook
- improve your proficiency with basic laboratory manipulations
- learn several common analytical techniques
- gain experience with the available hardware and software
- analyze real experimental data
- work on writing the sections of a formal lab report
- learn to work as an efficient team

Each of these experiments provides a list of skills to learn, as well as a reasonably detailed set of directions. Your goal for these experiments is to master these skills so that you can apply them to the more open-ended projects comprising the last two-thirds of the semester. Take careful notes (in your electronic notebook, of course) on the proper use of the software and hardware and the details of common analytical techniques. You will find these notes useful when completing later experiments. Even better, assign someone to be the group's expert for each task.

Lab reports for these experiments focus on specific sections of a formal report and are prepared as a group. For a general review of expectations, review the section of the lab manual entitled "Some Guidelines for Preparing a Formal Report" and examine the sample report in Appendix One. For each of these experiments a draft of the lab report is required. Assign one group member to prepare a first draft, providing copies to the remaining group members for comments, corrections and suggestions. Working together, prepare a joint second draft. Turn in the first draft, the copies of this first draft with comments and the second draft by the date provided during lab. After receiving your instructor's comments, prepare a single final report, which is due by the date provided in lab. Note – Your instructor's comments on drafts cannot address every fault in writing and reasoning; you should, therefore, review your entire draft for improvements. Don't assume that responding only to your instructor's comments will guarantee a polished final lab report.

Arriving on time for these experiments is crucial as we will use the first 20-30 to review the hardware and software being used.

Experiment One: Preparing Solutions

One of the most important laboratory skills is the ability to prepare solutions accurately and precisely. In your prior laboratory experiences, both in high school and at DePauw, most solutions were prepared for you, or the solutions that you made did not have to be prepared to an exact concentration. This semester, however, you will prepare many solutions and you will need to do so with appropriate accuracy and precision. This is not a difficult task; it just requires patience and attention to detail.

The goal of this experiment is to successfully prepare three solutions, cleverly labeled Solution A, Solution B and Solution C. To do so you will need to complete some stoichiometric calculations, measure several reagents carefully using a balance or pipet, and dissolve these reagents in a solution of known volume using volumetric flasks. After preparing these solutions you will combine them with a fourth solution (which is provided to you) and observe the resulting reaction. If you prepare your solutions carefully you will see an interesting result. Before preparing these solutions, however, you will first evaluate the accuracy and precision of various methods for measuring volume.

Skills Emphasized In This Lab. By completing this lab you will become more comfortable with:

- measuring volume with appropriate accuracy and precision
- summarizing data using basic statistics, such as means and standard deviations
- preparing useful tables
- performing the stoichiometric calculations associated with preparing solutions
- making solutions
- maintaining an electronic notebook

Preparing for Lab. Before coming to lab read the following sections of the lab manual: "Accuracy, Precision and Analytical Measurements," "Measuring Mass" and "Measuring Volume." In addition, read the instructions for preparing the three solutions and complete all necessary calculations.

Evaluating the Accuracy and Precision of Glassware for Measuring Volume

As noted in the tutorial on "Measuring Volume," there are many ways to dispense a liquid reagent, each of which has its own inherent accuracy and precision. Generally, the more accurately or precisely you need to know the volume the more time it takes to make the measurement. For this reason you should carefully think about your need for accuracy and precision when choosing glassware.

In the first part of today's lab you will investigate the accuracy and precision of the glassware available to you by dispensing 10 mL of water, measuring its mass and converting that mass to its corresponding volume using water's known temperature-dependent density. Working with your partners, determine the accuracy and precision of

the following approaches to dispensing 10 mL of water: a 10-mL graduated cylinder, a 50-mL beaker, a 10-mL volumetric pipet and a 10-mL volumetric flask. The general procedure is described here for the 10-mL graduated cylinder:

1. Obtain 1-L of water from the reservoir supplied in lab, which is in equilibrium with the lab's temperature. Record the water's temperature and find its temperature-dependent density from the table in Appendix Three.
2. Dry a 100-mL beaker and record its weight.
3. Using your supply of water, dispense 10 mL using a 10-mL graduated cylinder. Weigh the beaker and water, determine the mass of water dispensed and calculate the volume.
4. Repeat Step 3 for a total of five trials.
5. Calculate the mean, standard deviation, relative standard deviation, and percent error (assuming a true value of 10 mL). Be sure to think about the number of significant figures that you can reasonably report for each of these values.

Repeat this procedure for the other approaches to measuring volume. Use Excel to record your data and to handle the necessary calculations, including finding means and standard deviations. Be sure to save this file to the appropriate location in your group folder and to create a hyperlink to the file in your electronic notebook. Include a brief analysis of your results. As a part of this analysis note which items of glassware are the most accurate, the least accurate, the most precise and the least precise.

Preparing the Solutions

Solution A is 50 mL of 0.23 M $KBrO_3$, which also is known as potassium bromate. Begin by calculating, to the correct number of significant figures, the grams of potassium bromate you will need. Weigh out the correct amount of $KBrO_3$ and carefully bring it back to your lab bench. Transfer the $KBrO_3$ to a 50-mL volumetric flask and dilute to volume with deionized water. Transfer the solution to a clean, dry and labeled beaker. Cover the beaker and save it for later.

Solution B is 50 mL of a mixture containing 0.31 M $CH_2(COOH)_2$, also known as malonic acid, and 0.059 M KBr, which is potassium bromide. Following the general approach to preparing Solution A, add both solids to the volumetric flask and dilute to volume with deionized water. Transfer the solution to a clean, dry and labeled beaker. Cover the beaker and save it for later.

Solution C is 50 mL of a mixture consisting of 0.019 M cerium (IV) and 2.7 M H_2SO_4, or sulfuric acid. Begin by preparing 100 mL of 2.7 M H_2SO_4 using the available solution of 42.3% w/w H_2SO_4. This concentration unit, which may be less familiar to you, is called a weight-to-weight percent (100 g of the solution contains 42.3 g of H_2SO_4). The density of 42.3% w/w H_2SO_4 is 1.25 g solution/mL solution. Calculate the required volume, in mL, of 42.3% w/w H_2SO_4 and, using a graduated cylinder, slowly add it to a 100-mL volu-

metric flask that already contains approximately 25 mL of deionized water. Dilute to volume with deionized water and mix thoroughly.

Cerium is obtained using cerium (IV) ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$, which is available as a solid. Following the general approach to preparing Solution A, use your solution of 2.7 M H_2SO_4 to transfer the $Ce(NH_4)_2(NO_3)_6$ to the 50-mL volumetric flask and dilute to volume using your 2.7 M H_2SO_4. When complete, transfer the solution to a clean, dry and labeled beaker. Cover the beaker and save it for later.

Did You Prepare the Solutions Carefully?

Now comes the moment of truth! Obtain a clean 250-mL beaker, a magnetic stirrer and a stir bar. Pour all of solutions A and B into the beaker and adjust the stirrer to produce a small vortex (a little solution tornado). If the solution develops an initial amber color, then wait until it turns colorless before proceeding; this is not a common occurrence. When the solution is colorless, add, at the same time, all of solution C and 3 mL of the already prepared Solution D (measured using a graduated cylinder). Examine the resulting reaction for several minutes, observing the interesting and spectacular results. You will have no trouble deciding if your solutions were prepared carefully. Be sure to have your instructor or TA verify your success and to record your observations in your electronic notebook.

Cautions. There are no cautions for this lab other than the normal respect for chemicals.

Waste Disposal

The reaction mixture can be flushed down the drain with plenty of water.

Lab Report

Your electronic laboratory notebook serves as your report for this lab.

Experiment Two: Newton's Law of Cooling

A hot object in contact with a cooler environment loses heat by forced convection. The rate at which heat is lost is proportional to a number of factors, including the difference between the object's temperature and that of its surroundings. Mathematically, this relationship is known as Newton's Law of Cooling

$$\frac{dT(t)}{dt} = -K[T(t) - T_S]$$

where *T(t)* is the object's temperature at time *t*, T_S is the temperature of the surroundings, and *K* is a constant whose value depends upon the object's properties.

This form of Newton's law is hard to interpret as we generally aren't too adept at visualizing differential equations. Integrating the equation, however, shows us that temperature decreases exponentially with time

$$T(t) = T_S + (T_0 - T_S)e^{-Kt}$$

where T_0 is the object's original temperature. In this experiment you will examine the validity of Newton's law.

Skills Emphasized In This Lab. By completing this lab you will become more comfortable with:

- using the LoggerPro interface and software to collect and analyze data
- using regression to fit a theoretical equation to experimental data
- preparing useful figures for reporting data
- communicating the results and conclusions of your work to others through a written report

Preparing for Lab. Be sure to review the "How To…" files on the course's web-page for instructions on using the LabPro interface and the LoggerPro software, and to complete the appropriate sections of your electronic notebook before coming to lab.

Procedure. Begin by heating 500 mL of deionized water to a temperature between 50°C and 100°C. Connect the LoggerPro interface to your computer and insert the temperature probe. Launch the LoggerPro software and set your data acquisition parameters for a time-based experiment lasting five minutes with a sampling rate of 30 points per minute.

When the water in your beaker is within the desired range, place the temperature probe in the water and allow it to equilibrate for at least one minute. Remove the probe, wipe off any residual water with a Kimwipe and suspend the probe in the air using a stand and clamp. Click on LoggerPro's ***Collect*** button to initiate data collection. When the data col-

lection is complete be sure to store your data before continuing. Repeat this procedure for a minimum of seven trials. Do not try to begin these trials at the same initial temperature; in fact, it is best if you have a range of initial temperatures between 50^oC and 100^oC.

Repeat using your second temperature probe.

Analyze the data for each trial by fitting a suitable equation (hint: try to match one of LoggerPro's built in functions to Newton's Law), determining values for T_0, T_s, and K.

Cautions. There are no serious cautions for this lab other than being careful when handling hot water.

Waste Disposal. This is easy – it's just water!

Lab Report. For this report, focus on the results and conclusions section only, paying particular attention to developing a narrative that uses tables and figures to summarize your data, that clearly analyzes your results and that reaches clearly stated conclusions. Be sure to review the guidelines for preparing reports and the sample report in Appendix One. Of particular interest is your determination of values for T_0, T_s, and K. At a minimum, your report should address the following questions: What are the expected values for the variables T_0, T_s and K, or are expected values unknown? If expected values of T_0, T_s and K are known, how accurate are your experimental results? How reproducible are your results for each variable and is this reproducibility (or lack or reproducibility) expected? Is Newton's Law obeyed for the cooling of a hot probe and, if not, can you explain why? It might help to do some research on Newton's law, particularly with respect to its limitations and/or assumptions. Limit this report to two or three pages of double-spaced text, not counting any space used for figures or tables.

Experiment Three: Determining the Amount of Acetic Acid in Vinegar

Vinegar is a dilute solution of acetic acid, CH_3COOH, that, according to the FDA, should contain at least 4.0 g of acetic acid per 100 mL of solution.[1] Because acetic acid is a weak acid, its concentration in any solution, including vinegar, can be determined by reacting it with a strong base such as NaOH.

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

This is easily accomplished using an acid/base titration in which NaOH is the titrant. Because the reaction's stoichiometry is 1:1, the moles of NaOH used is equivalent to the moles of acetic acid in a vinegar sample of known volume. The concentration of acetic acid in vinegar is then easily calculated.

Skills Emphasized In This Lab. By completing this lab you will become more comfortable with:

- using the LoggerPro interface to calibrate and use a pH electrode
- performing an automated titration using the LoggerPro interface and the Vernier drop counter
- standardizing a solution by an acid/base titration
- learning to extract equivalence points from titration curves
- writing a succinct procedure that provides an experienced scientist with enough information to duplicate your work

Preparing for Lab. Be sure to review the "How To…" files on the course's web-page for instructions on using the Vernier Drop Counter. In addition, you should review the section in the lab manual on "Acid/Base Titrations." Be sure to complete the appropriate sections of your electronic notebook before coming to lab.

Procedure. Begin by preparing 300 mL of approximately 0.1 M NaOH by transferring an appropriate amount of NaOH into a beaker and dissolving in 300 mL of deionized water. Because NaOH is not available in a pure form, the exact concentration of this solution cannot be determined from the mass of NaOH and volume of solution. Instead, you will determine the solution's concentration by titrating it against the weak acid potassium hydrogen phthalate, $C_8H_5O_4K$, also known as KHP, which is available in a pure form. This process is called a standardization, the reaction for which is

$$OH^-(aq) + C_8H_5O_4^-(aq) \rightarrow H_2O(l) + C_8H_4O_4^{2-}(aq)$$

To complete the titration, set up and calibrate the Vernier drop counter. Fill the reservoir with your solution of nominally 0.1 M NaOH. Transfer approximately 0.3 g of KHP into a small beaker and dissolve in approximately 50 mL of deionized water (you may gently

[1] http://www.fda.gov/ora/compliance_ref/cpg/cpgfod/cpg525-825.html (checked August 2006).

heat the solution if the KHP is difficult to dissolve, but you must allow it to cool to room temperature before continuing). Calibrate your pH electrode and suspend it in the solution of KHP, ensuring that the sensing bulb is fully immersed. Add a small stir bar and gently stir the solution. Begin the titration and continue until you obtain a complete titration curve. Locate the equivalence point and calculate the molarity of your NaOH solution.

To analyze vinegar for its concentration of acetic acid, pipet 2 mL of vinegar into a small beaker and add enough deionized water to cover the pH electrode's sensing bulb when it is suspended in the beaker. Gently stir the solution and titrate the sample with your NaOH until you obtain a complete titration curve. Locate the equivalence point and calculate the %w/v acetic acid in the vinegar.

To ensure that you have sufficient data for both the standardization of NaOH and the analysis of vinegar, alternate between these two titrations. Gather as much data as you can by the end of the lab period.

Cautions. There are no cautions for this lab other than the normal respect for chemicals.

Waste Disposal. All solutions may be disposed of down the drain with copious amounts of water.

Lab Report. For this report, focus on the procedure section only, limiting yourself to an absolute maximum of one double-spaced page. Be sure to review the guidelines for preparing reports and the sample report in Appendix One. When submitting the final report, please turn in a one-page summary of your results. This summary should clearly document the standardization of your NaOH solution and your analysis for the %w/v of acetic acid in vinegar. Use tables to organize your data and results. Remember that these tables must contain sufficient information to allow verification of your results.

Experiment Four: Characterizing an Oscillating Reaction

In the first week of lab you prepared three solutions, combined them with a fourth solution and observed the resulting reaction. This interesting reaction, which is known as the cerium-catalyzed Belousov-Zhabotinsky reaction, is one of a class of reactions that oscillate between different chemical states. Chemical reactions usually proceed smoothly from reactants-to-products with the concentrations of reactants steadily decreasing and the concentrations of products steadily increasing. In an oscillating system of reactions, however, one (or more) of the reactants eventually begins to increase in concentration, returning the system to a state similar to the initial set of conditions. Oscillations continue for minutes to hours but eventually cease when the concentration of one (or more) of the reactants falls below some critical level.

The cerium-catalyzed Belousov-Zhabotinsky reaction is complex, consisting of as many as 80 individual steps involving 26 different species! At its simplest level, the net reaction is the bromination of malonic acid; thus, the reaction's overall stoichiometry is

$$2H^+ + 2BrO_3^- + 3CH_2(COOH)_2 \rightarrow 2BrCH(COOH)_2 + 4H_2O + 3CO_2$$

Skills Emphasized In This Lab. By completing this lab you will become more comfortable with:

- using the Ocean Optics Chem 2000 Spectrometer and OOIChem software
- preparing a set of calibration standards and verifying Beer's law
- writing a thorough introduction that provides a succinct background to your lab work and clearly outlines the goals of your work

Preparing for Lab. Familiarize yourself with the hardware (Ocean Optics Chem2000 Spectrometer) and software (OOIChem) used in this experiment by reviewing the "How To…" documents on the course's web site. Pay particular attention to exporting data from OOIChem to a more useful program, such as Excel or Graphical Analysis. In addition, read the section in the lab manual on "Visible Absorbance Spectra and Beer's Law." Be sure to complete the appropriate sections of your electronic notebook before coming to lab.

Procedure. The goal of this week's lab is to characterize the oscillations in the cerium-catalyzed Belousov-Zhabotinsky reaction using a computer-interfaced spectrometer. Because several components of the system are colored, the reaction can be followed by monitoring the solution's absorbance as a function of time. Properties of the oscillating reaction that you might find of interest include the oscillation's magnitude and period and how they change as the reaction progresses, whether there is a difference in the oscillations at different wavelengths and the reproducibility of the oscillations from trial-to-trial.

To save time, all solutions have been prepared for you. For this lab, the standard run will consist of 25 mL each of solutions A, B and C, and 1.5 mL of ferroin (Solution D). Use graduated cylinders to measure the appropriate volumes of solutions A, B, and C, and a

disposable plastic pipet for the ferroin solution. Be sure to follow the correct order for mixing the reagents as outlined in Experiment One.

Before monitoring the reaction, you will first verify that absorbance provides a direct measure of concentration; that is, you will verify that Beer's law applies to Solution C, which is yellow due to the presence of Ce(IV), and to Solution D, which is red due to the presence of $Fe(o\text{-phenanthroline})_3^{2+}$. Begin by adding 25 mL of Solution C to 50 mL of deionized water; this working solution has a concentration of Ce(IV) similar to that at the beginning of the reaction. Set up the Ocean Optics spectrometer and record the spectrum of your dilute solution of Ce(IV) using deionized water as your reference. Adjust the signal acquisition parameters to obtain a reasonably smooth spectrum over the range of wavelengths from 390 nm to 900 nm. When you are satisfied with your spectrum, select a wavelength where the solution's absorbance is strong but not noisy and record the absorbance.[1]

Next, prepare a series of standard solutions of Ce(IV) by pipeting 5, 10, 15, and 20 mL of your working solution of Ce(IV) into separate 25-mL volumetric flasks, diluting each to volume using deionized water. Measure the absorbance of these four solutions at your previously selected wavelength. Verify Beer's law by constructing a plot of absorbance vs. [Ce(IV)]; you should have a total of six points on this graph, one of which is your reference.

Thoroughly rinse your glassware and repeat this verification of Beer's law for ferroin using a working solution containing 1.5 mL of Solution D and 75 mL of deionized water.

After verifying Beer's law for Ce(IV) and ferroin, initiate the oscillating reaction, transfer a portion of the reaction mixture to a cuvette and follow the reaction's changing colors using the spectrometer. For your first trial, simply observe the changes in the solution's spectrum as the reaction progresses and select two to four wavelengths where there is an oscillation in absorbance. Try to select wavelengths corresponding to each of the oscillating reaction's most obvious colors.

After selecting your wavelengths, discard the reaction mixture and initiate a new oscillating reaction. This time use OOIChem's kinetics mode to monitor the reaction at the wavelengths identified earlier. Set the sampling rate to one point per second and monitor the reaction for 15 minutes or until the oscillations stop, whichever is shorter. Repeat for at least one additional trial.

Cautions. There are no cautions for this lab other than the normal respect for chemicals.

Waste Disposal. Pour any remaining solutions together. The resulting mixture can be flushed down the drain with plenty of water.

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[1] Normally it is best to monitor absorbance at the wavelength with the greatest absorbance, but this is not possible for solutions that are yellow as they absorb most strongly at wavelength's beyond the reach of the spectrometer's detector.

Lab Report. For this report, focus on the introduction only. Research has a purpose and its context forms the basis for the introduction. Choose one of the following contexts and use it to develop your introduction:

- After attending a seminar by Boris Belousov, in which he describes his discovery of an oscillating reaction and its rejection by the scientific community, you decide to gather spectrophotometric evidence to support Belousov's discovery.
- Although the scientific community accepts the B-Z reaction, the reaction's mechanism remains controversial. You believe that the oscillating colors are due to Ce(IV), $Fe(o\text{-}phen)_3^{2+}$ and $Fe(o\text{-}phen)_3^{3+}$ and decide to study this spectrophotometrically.
- The scientific community has come to agreement on a mechanism for the B-Z reaction. Changes in the reaction's oscillations with time, however, have not been studied; you decide to fill this gap.

Be sure to review the guidelines for preparing reports and the sample report in Appendix One. Limit this introduction to two or three pages of double-spaced text, not counting space used for reactions or equations, and include a minimum of three references, one of which must be Winfree, A. T., "The Prehistory of the Belousov-Zhabotishky Oscillator," *J. Chem. Educ.* **1984**, *61*, 661-663 (available in Prevo and through electronic access; see library for details). Be sure to state clearly which prompt you are using.

When submitting your final report, append neatly prepared figures showing the calibration curves for Ce(IV) and for ferroin, and the reaction's oscillations. These figures should satisfy the guidelines for figures outlined elsewhere in this manual.

Open-Ended Project Experiments

The purpose of the last four experiments, each of which lasts two or three weeks, is to provide you with the opportunity to design and carry out your own experiments. Each experiment begins with a brief description of the system under investigation, a statement of the project's goals and a list of hints, suggestions, and/or questions to consider. These experiments build upon the skills learned during the preliminary experiments, so you will find it useful to look back at your earlier work.

For each of theses project experiments you will prepare a formal group report. Details on these reports are included with each experiment.

Success with these experiments depends on good planning, both before beginning work in the lab and between lab periods. Be sure to reserve time outside of lab for your group to meet and make plans.

Experiment Five: Thermodynamics of Hydrogen Peroxide's Decomposition

At the beginning of the term we discussed and observed the decomposition of hydrogen peroxide in the presence of Fe^{3+}. The reaction's stoichiometry, interestingly, does not include Fe^{3+}

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

but does result in the release of energy in the form of heat. The purpose of this two-week, open-ended project is to design and carry out suitable experiments that can provide answers to the following questions:

- Does the absolute amount of heat produced during any given reaction depend on the quantity of hydrogen peroxide or Fe^{3+} used?
- Can you demonstrate experimentally that the role of Fe^{3+} in this reaction is catalytic?
- What is the value of ΔH for the reaction?

Preparing for Lab. Planning for this lab is critical to your success. Be sure to complete the relevant sections of your notebook before each week's lab session. As you develop strategies for exploring and answering the questions posed above, keep the following in mind:

- To determine whether there is a relationship between two variables you must ensure that all other variables in the experiment remain fixed.
- A calorimeter will absorb some of the heat released in an exothermic reaction (that is, a calorimeter is not a perfect insulator). You need to establish if the amount of heat absorbed by your calorimeter is significant and, if so, determine how to correct for its contribution to your experimentally determined value for ΔH. *Hint: try looking for information about calorimeter constants.*
- Be sure to investigate the properties of a catalyst and to consider several ways to verify that Fe^{3+} is serving as a catalyst.
- In determining a value for ΔH you will inevitably make some assumptions. Give this some thought and try to minimize the number of assumptions you must make. When an assumption is necessary, consider how it might affect your results.
- Experimentally determined values should be compared to expected theoretical values and any significant differences explained.

When asked, you should be prepared to discuss your thoughts on these points during lab.

Procedure. Stock solutions of H_2O_2 and $Fe(NO_3)_3$ are available in lab (the exact concentrations will be provided after the solutions have been made). These solutions can be diluted as needed. Calorimeters also will be provided.

Cautions. The decomposition of hydrogen peroxide is reasonably exothermic and, depending on your experimental conditions, can produce solutions with temperatures near or above 60^{o}C. Additionally, the rapid formation of O_2 can produce enough pressure to shoot the hot contents out through the small holes in your calorimeter's lid (kind of like a geyser at Yellowstone National Park). *It is a good idea to first try any reaction without placing a lid on your calorimeter, observing the approximate change in temperature and noting how vigorous the reaction is.* Be careful and **WEAR YOUR SAFETY GLASSES AT ALL TIMES.**

Waste Disposal. All solutions may be disposed of down the drain with copious amounts of water.

Lab Report. In preparing a formal report, please follow the guidelines found elsewhere in this manual, limiting your report to a maximum of six pages of text (not including reactions, equations, figures or tables). Attach a completed copy of the "Checklist for Formal Reports" to your report. You are encouraged to discuss with me your report; however, I will not be able to review drafts.

Experiment Six: Thermodynamics and Solubility of Calcium Hydroxide

We usually view thermodynamics and equilibrium chemistry as providing very different types of information about a chemical reaction. For example, when we consider a reaction thermodynamically we often ask "Is this reaction likely to occur?" and then calculate ΔG and make a prediction. As we will see in class, when considering equilibrium chemistry, we usually ask "What is the composition of this reaction mixture when it reaches equilibrium?" and then use the reaction's equilibrium constant, the mixture's initial composition and the reaction's stoichiometry to make a prediction. What is often neglected, however, is the relationship between these two views of chemical reactivity. After all, the standard state free energy (ΔG^o) and the equilibrium constant (K_{eq}) are related by the equation

$$\Delta G^o = -RT\ln K_{eq}$$

showing that thermodynamics and equilibria provide complementary information for a reaction. We can, for example, use a reaction's equilibrium constant and the reaction mixture's reactant quotient, Q, to predict the favorable direction for a reaction, and we can use the free energy at any moment during the reaction's progress to determine the reaction's composition.

The purpose of this two-week, open-ended project is to study the thermodynamics for the solubility of $Ca(OH)_2$

$$Ca(OH)_2(s) \leftrightarrows Ca^{2+}(aq) + 2OH^-(aq)$$

for which the equilibrium constant (also called the solubility product) is

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

More specifically, you should design and carry out suitable experiments that can provide answers to the following questions:

- How does the solubility of $Ca(OH)_2$ change with temperature?
- What are the values for ΔG^o, ΔH^o and ΔS^o for $Ca(OH)_2$?

Preparing for Lab. Planning for this lab is critical to your success. Be sure to complete the relevant sections of your notebook before each week's lab session. As you develop strategies for determining values ΔG^o, ΔH^o and ΔS^o, keep the following in mind:

- Because the solubility reaction releases a base, OH^-, you can use an acid/base titration to determine the concentration of OH^- in a saturated solution of $Ca(OH)_2$.

- To determine the concentration of OH^- in a saturated solution of $Ca(OH)_2$ you must first remove any undissolved $Ca(OH)_2$ by filtering. Consider why this is necessary and what complications might arise if you don't successfully remove all the $Ca(OH)_2$.
- To determine the concentration of OH^- in a saturated solution of $Ca(OH)_2$ you will need a solution of HCl whose nominal concentration is 0.01 M. You will need to determine, therefore, how to prepare a suitable amount of this solution using the available stock solution of nominally 1 M HCl. You will determine the concentration of your solution of HCl by titrating it against the standard weak base tris(hydroxymethyl)aminomethane, which is usually called TRIS or THAM; you may take the reaction to be

$$TRIS + HCl \rightarrow TRISH^+ + Cl^-$$

  The chemical formula for TRIS is $(HOCH_2)_3CNH_2$ and it is available as a solid.
- Review your preparation and standardization of a standard solution of NaOH in Experiment 3 and adapt that procedure to this lab. Plan on each titration requiring about 15 mL of titrant to reach the equivalence point. If your first titration requires significantly less than or significantly more than 15 mL, then make suitable adjustments to your procedure. To determine how much HCl to make, consider how many total titrations you will make in two weeks and assume that each will require 30 mL of HCl; double this total and you should be fine.
- You need to decide how many mL of filtered $Ca(OH)_2$ to use in your titrations. As a "rule of thumb," your room-temperature titrations should use approximately 15 mL of your nominally 0.01 M HCl to reach their equivalence points. You might find it helpful to know that the solubility of $Ca(OH)_2$ is reported to be about one gram per liter of water. If your first titration requires significantly less than or significantly more than 15 mL, then make suitable adjustments to your procedure.
- You need to decide how to calculate ΔG^o using data from your titrations. *Be sure that you consider this before you begin gathering data so that you know the accuracy and precision needed for different measurements.*
- It is possible to determine values for ΔH^o and ΔS^o by studying the solubility of $Ca(OH)_2$ at several temperatures; give some thought to how this is done.
- Experimentally determined values should be compared to their expected theoretical values.

When asked, you should be prepared to discuss your thoughts on these points during lab.

Procedure. Your first task, of course, is to prepare and standardize your solution of HCl. Once this is completed you may begin analyzing samples. During the first week you will be provided with a room-temperature saturated solution of $Ca(OH)_2$. Samples drawn from this supply may be filtered by gravity filtration. During the second week you will be provided with a saturated solution of $Ca(OH)_2$ at an elevated temperature. As this solution cools during the lab period you can extract and analyze samples. Samples drawn

from this supply will be filtered by syringe filtration (this method of filtration will be demonstrated in lab).

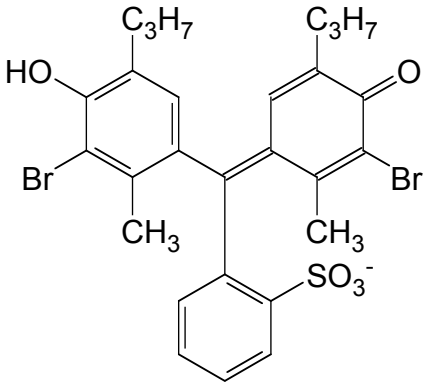
Cautions. There are no cautions for this lab other than the normal respect for chemicals and the need to safely handle hot solutions.

Waste Disposal. All solutions can be disposed of down the drain, flushing with copious amounts of water.

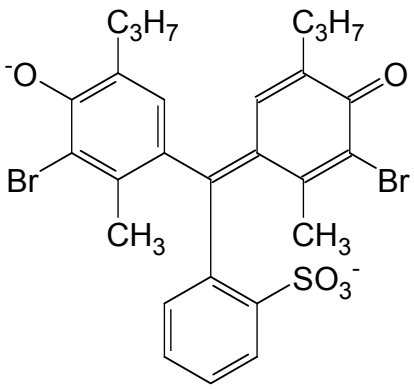
Lab Report. In preparing a formal report, please follow the guidelines found elsewhere in this manual, limiting your report to a maximum of six pages of text (not including reactions, equations, figures or tables). Attach a completed copy of the "Checklist for Formal Reports" to your report. You are encouraged to discuss with me your report; however, I will not be able to review drafts.

Experiment Seven: Acid Dissociation Constants for Organic Dyes

One of the simplest methods for estimating the pH of a solution is to add a small amount of an organic dye and observe the solution's resulting color. For example, solutions of bromothymol blue, which is one member of the class of sulfonophthalein dyes, are yellow at pH levels less than 6 and blue for pH levels greater than 8. This change in color occurs because bromothymol blue is a weak acid whose degree of ionization depends on pH. At a pH of 5, for example, bromothymol blue is present in its weak acid form, which has the structure shown to the right.



Adding a strong base removes the proton from the -OH functional group on the upper left ring, leaving the conjugate weak base shown to the left. At pH levels between 6 and 8, solutions of bromothymol blue shift from yellow to blue, passing through various shades of yellow-green, green, and green-blue that can be correlated to within a few tenths of a pH unit.



The relationship between the color of a solution of bromothymol blue (that is, its ability to absorb visible light at a given wavelength) and pH, as described above, is intuitively obvious if you remember the basics of mixing colors. Less obvious is the exact mathematical relationship between absorbance and pH

$$\log\left(\frac{A - A_{In^-}}{A_{HIn} - A}\right) = pK_a - pH$$

where A is the absorbance at a particular pH and A_{In^-} and A_{HIn} are the absorbance values for the weak base and weak acid forms, respectively. Note that this equation suggests it is possible to determine a dye's pK_a by monitoring its absorbance as a function of pH.

The purpose of this two-week, open-ended project is to design and carry out suitable experiments that can provide the pK_a value for two organic dyes. Specifically, you will

- determine the pK_a of bromocresol green, a commercially available synthetic organic sulfonophthalein dye used as a visual indicator in acid/base titrations
- determine the pK_a of neutral red, a commercially available synthetic euhodin dye used as a visual indicator and as a stain in histology

Preparing for Lab. Planning for this lab is critical to your success. Read the following paper as it provides useful information for determining the pK_a value for organic dyes.

> Patterson, G. S. "A Simplified Method for Finding the pK_a of an Acid-Base Indicator by Spectrophotometry" *J. Chem. Educ.* **1999**, *76*, 395-398.

You can retrieve an electronic copy of this paper from the workshop folder on the course's I-drive. Be sure to complete the relevant sections of your notebook before each week's lab session. As you develop strategies for determining the dye's pK_a value, keep the following in mind:

- The paper provides complete experimental details for determining the pK_a of bromophenol blue and sufficient information to help you design a procedure for determining the pK_a of bromocresol green. You will need to adapt the procedure to determine the pK_a for neutral red.
- The work described in the paper uses a different instrument for acquiring absorbance spectra and for measuring absorbance. You will need to obtain the same information using the Ocean Optics USB2000 spectrometer and, therefore, need to modify the published procedure to fit our equipment. Be sure to review the instructions for using the spectrometer and its associated software.
- One shortcoming of the paper is that the author did not verify Beer's law; that is, the author did not show that absorbance is a linear function of concentration. Be sure to verify that Beer's law applies to both dyes. Review how you did this in an earlier lab and adapt that approach to this lab.
- You will need to complete some research on each dye. Among the information that you may find useful are structures, the expected color of the weak acid and weak base forms and approximate pK_a values.
- Table 5 in the paper provides published pK_a values for three ionic strengths. Do some research into the topic of ionic strength to understand what it is, how it is calculated and why the author includes it in his paper. Think about how to estimate the ionic strength of your solutions.
- Any experimentally determined values should be compared to their expected theoretical values.

When asked, you should be prepared to discuss your thoughts on these points during lab.

Procedure. During the first week you should plan to work on determining the pK_a value for bromocresol green. During second week you will determine the pK_a for neutral red.

Cautions. There are no serious cautions for this lab other than the normal respect for chemicals.

Waste Disposal. All solutions can be disposed of down the drain, flushing with copious amounts of water.

Lab Report. In preparing a formal report, please follow the guidelines found elsewhere in this manual, limiting your report to a maximum of six pages of text (not including reactions, equations, figures or tables). Attach a completed copy of the "Checklist for Formal Reports" to your report. You are encouraged to discuss with me your report; however, I will not be able to review drafts.

Experiment Eight: Kinetics of the Bleaching of Dyes

Thermodynamics allows us to predict whether a reaction is favorable but does not inform us of the likelihood that the reaction will occur in a reasonable amount of time. To know something about the conditions favoring a timely reaction one must study the reaction's kinetics.

The relationship between a reaction's rate and the concentrations of species affecting the rate is given by a rate law, which takes the general form

$$\text{rate} = k[\text{A}]^{\alpha}[\text{B}]^{\beta}\cdots[\text{E}]^{\varepsilon}$$

where k is the rate constant and A, B and E are species whose concentration might affect the reaction's rate. The superscript associated with each concentration term (e.g. α, β and ε) are called reaction orders and may be positive or negative integers; they may even be zero or fractional.

In this two-week, open-ended experiment you will investigate the kinetics of the reaction responsible for the effectiveness of bleach. Commercial bleaches are solutions containing one or more oxidizing agents. One of the most common oxidizing agents in bleach is the hypochlorite ion, OCl^-, which usually is added in the form of its sodium salt, NaOCl, typically at a concentration between 5 and 6 % w/v.

Bleaches work by oxidizing stains, converting the compound responsible for the stain to a colorless product. Most stains are just colored organic compounds; thus, we will substitute an aqueous organic dye (blue food coloring) as a model stain compound. The overall reaction, then, simplifies to

$$\text{dye} + OCl^- \rightarrow \text{colorless product}$$

and the rate law for the reaction can, as a first estimate, be written as

$$\text{rate} = k[\text{dye}]^{\alpha}[OCl^-]^{\beta}$$

The goal of this study is to characterize the factors affecting the rate of this reaction. More specifically, you will

- determine the rate law for the reaction, including the reaction orders α and β, and the value of the rate constant, k
- study the possible effect of pH on the rate law

Preparing for Lab. Planning for this lab is critical to your success. Be sure to complete the relevant sections of your notebook before each week's lab session. As you develop strategies for determining the reaction's rate law keep the following in mind:

- As the reaction proceeds the solution will fade from its initial blue color to a colorless solution. You can follow the reaction's kinetics, therefore, by monitoring the solution's absorbance as a function of time. To use absorbance in place of concentration, however, you must establish that Beer's law applies to your solution of dye. You may wish to review your work from earlier labs to see how you have accomplished this. In addition, to obtain smooth kinetic data you need to minimize the noise in your absorbance spectra. Review how you accomplished this in an earlier lab.
- To study a reaction's kinetics you must ensure that the concentration of only one reactant is changing; that is, you will study the reaction under what is called a pseudo-order condition in which the initial concentration of dye is significantly smaller than the initial concentration of OCl^-. You should do some preliminary reading in your textbook to familiarize yourself with how pseudo-order kinetics work and verify that the rate law under these conditions is

$$\text{rate} = k_{obs}[\text{dye}]^{\alpha}$$

with an observed rate constant, k_{obs}, of

$$k_{obs} = k[OCl^-]^{\beta}$$

- You need to verify that the initial concentrations of dye and OCl^- are suitable for a pseudo-order kinetic study. The dye's molar absorptivity is 1.38×10^5 M^{-1} cm^{-1} at a wavelength of 630 nm. To determine the concentration of OCl^- in bleach you may adapt the following general redox titrimetric approach:

  Pipet 1 mL of bleach into a suitable flask and add approximately 50 mL of deionized water and 2 g of KI. Swirl the solution to dissolve the KI and then add approximately 3 mL of 3 M H_2SO_4. The resulting solution will be brown due to the formation of I_2, as shown by the following reaction

$$OCl^-(aq) + 2I^-(aq) + 2H_3O^+(aq) \rightarrow I_2(aq) + Cl^-(aq) + 3H_2O(l)$$

  Determine the amount of I_2 produced by titrating with a solution of $Na_2S_2O_3$ of known concentration using the ORP probe to monitor redox potential as a function of the volume of titrant. Redox titration curves are analyzed in the same manner as acid/base titration curves; review the tutorial on "Acid/Base Titrations" and your earlier standardizations of NaOH and HCl for further details. The titration reaction is

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

- You need to determine how kinetic data consisting of absorbance as a function of time can be used to determine the reaction order, α, for the dye and the reaction's observed rate constant, k_{obs}.
- You need to think about how kinetic runs using different initial concentrations of OCl^- can be used to extract information about the reaction order, β, for OCl^- and the reaction's true rate constant, k. Consider, as well, how you might prepare solutions of OCl^- with different concentrations.
- Because OCl^- is a weak base it is reasonable to expect that pH might affect the reaction's rate. Give some thought to reasonable pH levels to investigate and how you might set up a suitable kinetic experiment. Note – the reported pK_a values for blue food coloring are 5.63 and 6.85.

When asked, you should be prepared to discuss your thoughts on these points during lab.

Procedure. To prepare your dye solution, try adding 18 drops of dye to a liter of deionized water and then adjust the concentration so that the solution's maximum absorbance is between 0.8 and 1.0.

All kinetic runs should consist of 25 mL of a dye solution and 1 mL of a bleach solution. Be sure to begin data acquisition the moment the bleach is added and then transfer a portion of the solution to the spectrometer as soon as possible. Collect data until the absorbance reaches zero or a steady-state value.

Cautions. There are no serious cautions for this lab other than the normal respect for chemicals.

Waste Disposal. All solutions can be disposed of down the drain, flushing with copious amounts of water.

Lab Report. Details on this group report will be distributed separately.

Appendix One: Sample Report

Writing a formal report is always a challenge, particularly when you are uncertain about what should and should not be included. The purpose of this sample report is to provide you with an example of a typical report. Like any example, of course, this report cannot anticipate every issue you might encounter during the semester; it does provide, however, a sense of how to construct a report. The comments below provide some additional thoughts and observations.

Abstract – There are four things to note about the abstract: its short, it states the purpose of the experiment, it summarizes the experiment's two main results, and it compares one of the results to a theoretical value. As you prepare abstracts try to accomplish these three things.

Introduction – Your introduction must place the experiment within some context and define the experiment's goals. The context and goals, of course, are provided to you in the lab manual. For this experiment students were told that OCl^- is the active ingredient in bleach, that it is an oxidizing agent and that its release into the environment might be of concern. Students also were told that the experiment's goal was to determine the stoichiometry for the reaction between OCl^- and I^-. Students were given a copy of Job's paper on the method of continuous variations for metal-ligand complexes and asked to adapt that procedure to this experiment. In addition, because they had just completed a calorimetry experiment, the students were asked to use calorimetry in this experiment.

Note that this introduction accomplishes three things: it provides additional context for the experiment by citing references to the chemistry of OCl^- and relevant environmental concerns, and by discussing the difficulty of determining the stoichiometry of oxidation-reduction reactions (presumably the students did some research – note the references); it explains Job's method; and it clearly states the experiment's goals. Note, as well, that the first paragraph of the introduction begins with a "hook," which tells us why we should be interested in this research:

> "Although hypochlorite's reactivity with a wide variety of organic molecules is well known (*1*), particularly for organic dyes, its reactivity with inorganic ions has been studied less frequently. This is somewhat surprising given the significant release of OCl^- into the environment from household use (*2*)."

and that the final paragraph provides a transition to the rest of the report, telling the reader what is to come:

> "To evaluate the utility of the MCV as a method for studying oxidation-reduction chemistry, we present results for an analysis of the reaction between hypochlorite and iodide. A determination of the reaction's enthalpy provides further confirmation of the MCV results."

Procedure – The most striking observation about this procedure is the relative absence of numerical information. Note that the procedure makes no attempt to describe each individual experiment in detail. For example, carefully examine the first two sentences in the second paragraph and contrast the general information provided there with the more specific details included in the results and conclusions section.

Results and Conclusions – There are five things to note here. First, the results and conclusions are organized so that the reader can follow the logic of the data analysis. Note the use of subheadings as a means of focusing the reader's attention. Second, good use is made of tables and figures. Note, as well, that only representative results are provided. Third, results are reported clearly, including both means and standard deviations. Fourth, the main conclusions for each part of the experiment are clearly stated. Fifth, and finally, an analysis of error is included.

References – Note that the references are provided in the correct format. By the way, the reference to the paper by Job is real, although its title is fictitious. The remainder of the references are fictitious; your references, of course, will be real!

Notes – Many journals include a notes section to provide a place for comments and other information that would only clutter the main body of your text. Here the notes are used effectively to present sample calculations.

Appendices – Be sure to indicate what tables and figures in your I-drive account provide additional supporting information. Although I won't always look at them, I will if there are questions about your data.

A Thermodynamic Investigation of the Reaction Between Hypochlorite and Iodide

Abstract

The method of continuous variations and a calorimetric determination of enthalpy were used to verify the stoichiometry for the reaction between hypochlorite, OCl^-, and iodide, I^-. Stoichiometric mixing occurred with a 3:1 mole ratio between OCl^- and I^-, suggesting that the reaction is

$$3OCl^- + I^- \rightarrow IO_3^- + 3Cl^-$$

The experimentally determined value for ΔH of –344.4 kJ/mol$_{rxn}$ compares favorably with the expected value of –346.4 kJ/mol$_{rxn}$, providing further evidence that the proposed stoichiometry is correct.

Introduction

Hypochlorite ion, OCl^-, is a potent oxidizing agent commonly used in household bleaches. Although hypochlorite's reactivity with a wide variety of organic molecules is well known (*1*), particularly for organic dyes, its reactivity with inorganic ions has been studied less frequently. This is somewhat surprising given the significant release of OCl^- into the environment from household use (*2*).

One of the challenges in studying any reaction is determining the products. This is particularly problematic for oxidation-reduction reactions, such as those involving hypochlorite, because of the large number of possible oxidation states available to the oxidizing and reducing agents. For example, the chlorine in OCl^-, with an oxidation state of +1, can be reduced to oxidation states of 0 in Cl_2 and –1 in Cl^-, or oxidized to oxidation states of +3 in ClO_2^-, +5 in ClO_3^- and +7 in ClO_4^-. Although the identity of the product can be determined through standard chemical testing, this usually requires isolating individual species before using a standard qualitative analysis scheme.

The method of continuous variations (MCV), first described by Job (*3*) for the stoichiometric analysis of metal-ligand complexation, may provide a simple method for determining the stoichiometry of an oxidation-reduction reaction. The basis of MCV involves combining solutions of two reactants, A and B such that their combined moles, n_{tot}, remains constant in all experiments; thus

$$n_A + n_B = n_{tot}$$

where n_A and n_B are, respectively, the initial moles of A and B. The relative amount of each reactant can be expressed as a mole fraction, X

$$X_A = \frac{n_A}{n_{tot}}$$

$$X_B = 1 - X_A = \frac{n_B}{n_{tot}}$$

In a reaction between A and B, the extent of the reaction is determined by the limiting reagent. If an analytical signal is proportional to the limiting reagent, then a plot of that signal as a function of X_A will consist of two straight lines intersecting at a mole fraction of A, X_A, corresponding to the stoichiometric mixing of A and B. The mole ratio of A and B at this point is given by

$$\frac{n_A}{n_B} = \frac{X_A}{X_B} = \frac{X_A}{1 - X_A}$$

Figure 1 shows an MCV plot for a hypothetical reaction between the reactants A and B. The intersection at an X_A of 0.67 indicates that two moles of A stoichiometrically react with one mole of B, corresponding to a reaction of

$$2A + B \rightarrow \text{Products}$$

As noted by Job (*3*), there are three important limitations to the MCV: the reaction may involve only two reactants, there must be only one possible reaction and the free energy for the reaction must be highly favorable.

To evaluate the utility of the MCV as a method for studying oxidation-reduction chemistry, we present results for an analysis of the reaction between hypochlorite and iodide. A determination of the reaction's enthalpy provides further confirmation of the MCV results.

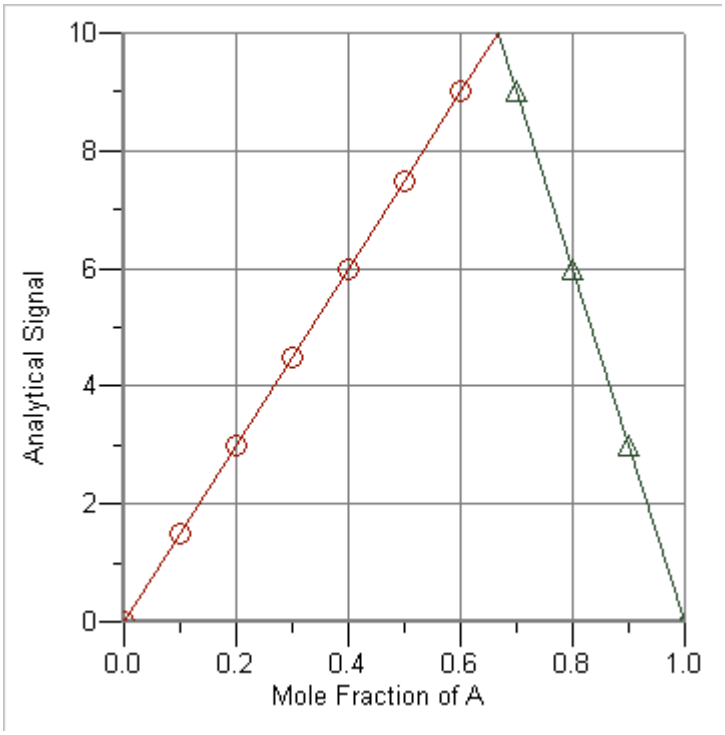


Figure 1. Hypothetical MCV plot for the reaction of A and B showing a stoichiometric mixing when the mole ratio of A to B is 2:1.

Procedure

All reactions were carried out in a locally designed cup calorimeter. Two small 8 oz. Styrofoam cups were nestled together and trimmed such that the inner cup did not protrude above the outer cup. The bottom of a 20 oz. Styrofoam cup was removed and used as a top. Two small holes were punched in the top to accommodate a digital thermometer connected to a LabPro data interface (Vernier) and a small glass funnel for adding reagents. Data were recorded and analyzed using LoggerPro (Vernier) on a Dell Latitude computer running Windows XP.

The calorimeter's suitability was tested by measuring the change in temperature when reacting 1.00 M solutions of HCl (Fisher Scientific) and NaOH (Fisher Scientific). The calorimeter's constant was determined using the method of Joule (*4)*, which is based on the thermal transfer of heat from hot water to cold water. In all calorimetric experiments, the temperature was monitored for several minutes both before and after adding the second solution to ensure that ΔT could be determined accurately by extrapolation.

Solutions of 0.213 M OCl^- and 0.213 M I^- were prepared from a commercial bleach (Kroger Brand) and reagent-grade KI (Fisher Scientific), respectively. The solution of KI also was 0.1 M in NaOH (Fisher Scientific). Both solutions were tightly capped when not in use. Calorimetry experiments for reactions involving OCl^- and I^- were limited to a combined volume of 80 mL. The reagent with the larger volume was initially placed in the calorimeter and the reagent with the smaller volume was then added. For those experiments used to establish the reaction's stoichiometry only the solution volumes were reported; the mass of each solution was measured in experiments used to determine ΔH.

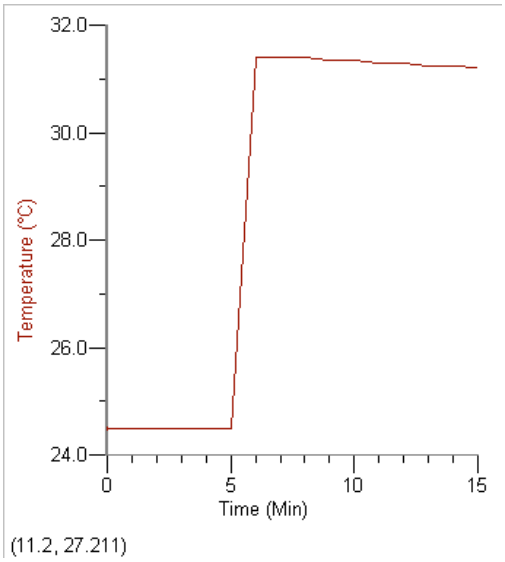


Figure 2. Temperature-time curve for 40 mL of hot water mixed with 40 mL of cold water.

Results and Conclusions

Evaluation of Calorimeter. The calorimeter's suitability for experiments based on the method of continuous variations was evaluated by measuring the temperature change upon mixing 40.0 mL of 1.00 M HCl with 40.0 mL of 1.00 M NaOH. Since ΔH^o for this reaction

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

is –55.836 kJ/mol_{rxn} the expected change in temperature is approximately 6.7 ^oC (Note 1). A typical result is shown in Figure 2 with ΔT being 6.9 ^oC. The mean ΔT for five trials was 6.8^oC with a standard deviation of 0.16^oC. The close agreement between the expected and experimental ΔT suggests that the change in temperature is a suitable means for studying the reaction.

Method of Continuous Variations. To establish the reaction's stoichiometry by the method of continuous variations, a series of calorimetry experiments were carried out in which the relative amounts of OCl^- and I^- were changed while maintaining a constant combined volume. Temperature-time curves for these experiments were similar to that shown in Figure 2 and are not included here. Table 1 and Figure 3 provide a summary of typical data.

Table I. Measurement of ΔT for Mixtures of OCl^- and I^-.

mL OCl^-	mL I^-	ΔT
10	70	0.7
20	60	1.5
30	50	2.2
40	40	2.9
50	30	3.7
60	20	4.4
70	10	2.2

Figure 3, which is a variation of the traditional MCV plot, shows that a stoichiometric mixing was achieved for the reaction of 60 mL of 0.213 M OCl^- with 20 mL of 0.213 M I^-. This corresponds to 1.28×10^{-2} mol OCl^- and 4.26×10^{-3} mol I^-, or a 3:1 molar ratio.

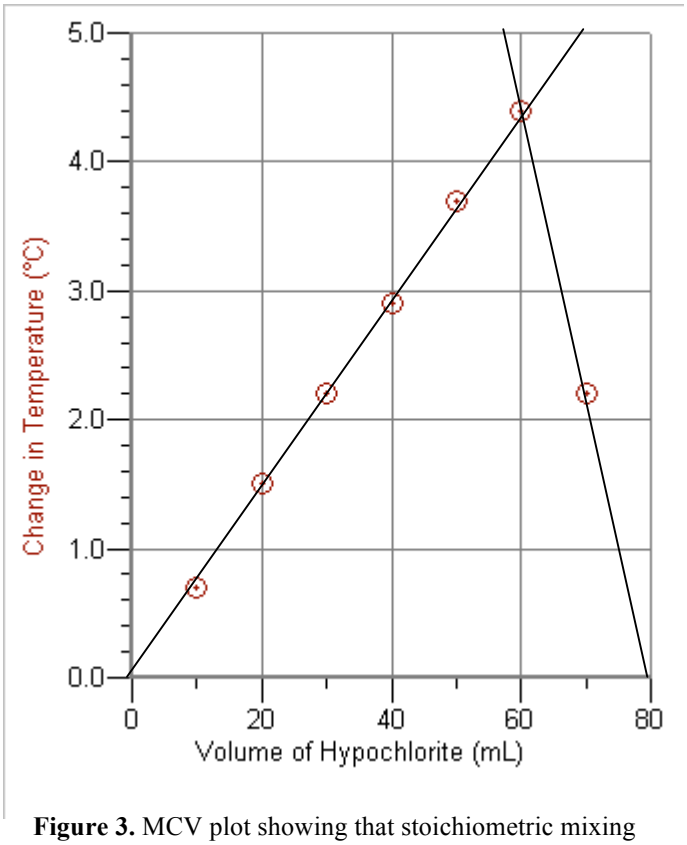


Figure 3. MCV plot showing that stoichiometric mixing occurs at 60 mL of hypochlorite and 20 mL of iodide.

Because iodine in I^- is in its most negative oxidation state, I^- must undergo oxidation. The chlorine in OCl^- must be reduced to either Cl_2 or Cl^-. If Cl_2 is the product, then a total of three electrons are needed to reduce the chlorine in the three OCl^- ions from oxidation states of +1 to 0. This requires the single I^- to experience a three electron oxidation from its initial oxidation state of –1 to a final oxidation state +2; however, no such oxidation state for iodine exists. If Cl^- is the reduction product, then a total of six electrons are needed to reduce the chlorine in the three OCl^- ions from oxidation states of +1 to –1. Oxidation of I^- to IO_3^- provides the necessary electrons. The proposed balanced redox reaction for this system, therefore, is

$$3OCl^- + I^- \rightarrow IO_3^- + 3Cl^- \qquad [1]$$

Calorimetric Determination of ΔH. To provide further evidence that the stoichiometry shown in Equation 1 is correct, additional experiments were run to determine the reaction's enthalpy, ΔH. The careful calorimetric measurement of a reaction's ΔH requires

determining the amount of heat absorbed by the calorimeter, q_{cal}. If the calorimeter's heat capacity, C_{cal}, is known then q_{cal} is given by

$$q_{cal} = C_{cal}\Delta T_{cal} \qquad [2]$$

where ΔT_{cal} is the calorimeter's change in temperature.

To evaluate the calorimeter's heat capacity approximately 40 g of room temperature water were placed in the calorimeter and the temperature monitored for several minutes to establish the initial temperature for both the water and the calorimeter. Approximately 40 g of hot water was then added to the calorimeter and the mixture's temperature monitored for several minutes. Conservation of energy requires that any heat lost by the hot water is absorbed by the room temperature water and the calorimeter; thus

$$-q_{hot} = q_{room} + q_{cal} \qquad [3]$$

Substituting Equation 2 and the equation for the heat flow for a solution into Equation 3 gives

$$-m_{hot}S_{hot}\Delta T_{hot} = m_{rt}S_{rt}\Delta T_{rt} + C_{cal}\Delta T_{cal}$$

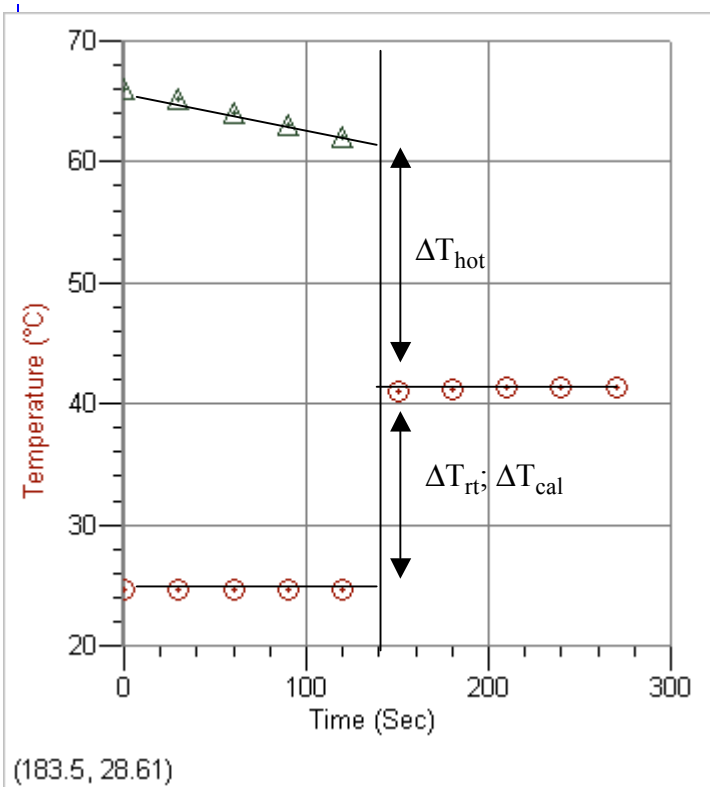


Figure 4. Typical temperature-time curve used to determine the calorimeter's constant.

where m is the water's mass and S is water's specific heat. Results for a typical run are shown in Figure 4, yielding a value of 31.5 J/°C for C_{cal} (Note 2). The average value of C_{cal} was found to be 31.4 J/°C with a standard deviation of 0.56 J/°C for three trials.

To determine ΔH_{rxn} additional calorimetry experiments were run using 60.00 mL of 0.213 M OCl^- and 20.00 mL of 0.213 M I^-. Results of these experiments are shown in Table 2.

Table 2. Calorimetry Results for the Reaction of 60.00 mL of 0.213 M OCl^- with 20.00 mL of 0.213 M I^-.		
mass of solution (g)	ΔT (^oC)	ΔH (kJ/mol_{rxn})
82.409	3.9	–344
82.616	3.8	–336
82.195	3.9	–344

The resulting mean and standard deviation for ΔH_{rxn} are –341 kJ/mol_{rxn} and 4.62 kJ/$mole_{rxn}$, respectively (Note 3). The theoretical value for ΔH_{rxn} is –346.4 kJ/mol_{rxn}, which gives an error of –1.8%. Because ΔT is known to only two significant figures the expected uncertainty in ΔH_{rxn} is ±10 kJ/mol_{rxn}, or a relative uncertainty of 2.8%. The experimental error of +1.8%, therefore, is reasonable and suggests that there are no significant problems with the experiment.

References

1. Ajax, V. *The Chemistry of Bleach*, Comet Press: New York, 1999.

2. "Environmentalist Expresses Concern Over Excessive Release of Bleach to Big Walnut Creek", http://www.bannergraphic.com/9.17.04/Bleach (accessed June 2006).

3. Job, P. "The Method of Continuous Variations for Studying Metal-Ligand Complexation" *Ann. Chim.*, **1928**, *9*, 113.

4. Joule, K. J. "Establishing the Calorimeter Constant by the Thermal Transfer of Energy From Hot to Cold Water" *J. Therm.* **1945**, *8*, 134.

Notes

1. The value of approximately 7^{o}C was determined as follows:

   a. Because equal moles of HCl and NaOH are mixed either reagent can be used as the limiting reagent. The moles of HCl used is 0.0400 moles.

   b. The amount of heat released, q_{rxn}, is

$$\frac{-55.836\ \text{kJ}}{\text{mol}_{\text{rxn}}} \times \frac{1\ \text{mol}_{\text{rxn}}}{\text{mol HCl}} \times 0.0400\ \text{mol HCl} \times \frac{1000\ \text{J}}{\text{kJ}} = -2233\text{J}$$

   c. The heat absorbed by the calorimeter, q_{cal}, is $-q_{rxn}$, or +2233 J.

d. The change in temperature is given by $q_{cal} = mS\Delta T$. Assuming that the combined solution has a density of 1.0 g/mL, the solution's mass is 80 g. Taking the specific heat as 4.184 J/g^{o}C, we have

$$+2233 \text{ J} = (80 \text{ g}) \times (4.184 \text{ J/g}^o\text{C}) \times \Delta T$$

gives ΔT as 6.7^{o}C. Note that no correction for the calorimeter's heat capacity was made as its influence is expected to be insignificant given the limit of one significant figure for the approximate temperature change.

2. The data in Figure 4 were obtained using 40.133 g of room temperature water and 39.168 g of hot water. Extrapolating the three temperature time curves to the point of mixing gives the initial temperature of the room temperature water and calorimeter as 24.7^{o}C, the initial temperature of the hot water as 61.5^{o}C and the mixture's final temperature as 41.3^{o}C. Thus, we find that ΔT_{rt} and ΔT_{cal} are 16.6^{o}C and ΔT_{hot} is -20.2^{o}C. Assuming that the solution's density is 1.00 g/mL and that the specific heat is 4.184 J/g^{o}C, we have

$$-(39.168 \text{ g})(4.184 \text{ J g}^{-1} \text{ }^o\text{C}^{-1})(-20.2 \text{ }^o\text{C}) =$$

$$(40.133 \text{ g})(4.184 \text{ J g}^{-1} \text{ }^o\text{C}^{-1})(16.6 \text{ }^o\text{C}) + C_{cal}(16.6 \text{ }^o\text{C})$$

which gives C_{cal} as 31.50 J ^{o}C^{-1}.

3. Outlined here are results for the data in the first row of Table 2. Applying the conservation of energy requires that

$$-q_{rxn} = q_{soln} + q_{cal}$$

where q_{rxn} is the heat supplied by the exothermic reaction and q_{soln} is the heat gained by the solution in the calorimeter; thus

$$-q_{rxn} = m_{soln}s_{soln}\Delta T_{soln} + C_{cal}\Delta T$$

Assuming that the solution's specific heat is the same as water gives

$$-q_{rxn} = (82.409 \text{ g})(4.184 \text{ J g}^{-1} \text{ }^o\text{C}^{-1})(3.9 \text{ }^o\text{C}) + (31.50 \text{ J } ^o\text{C}^{-1})(3.9 \text{ }^o\text{C}) = -1470 \text{ J}$$

Because this is a stoichiometric mixture the enthalpy change can be calculated using either OCl^- or I^-. Using OCl^-, for example, gives

$$\Delta H = q_{rxn}/n = -1470 \text{ J}/\{(0.213 \text{ M})(0.0600 \text{ L})\} \text{ x } 1 \text{ kJ}/1000 \text{ J} = -115 \text{ kJ/mol } OCl^-$$

where n is the moles of OCl^-. Accounting for hypochlorite's stoichiometry gives ΔH_{rxn} as

$$\Delta H_{rxn} = \Delta H \times (n_{LR})/\text{mol}_{rxn}$$

$$\Delta H_{rxn} = (3 \text{ mol } OCl^-/\text{mol}_{rxn})(-115 \text{ kJ/mol } OCl^-) = -340 \text{ kJ/mol}_{rxn}$$

Appendices

The following supplemental information is available in the experiment's folder on our I-drive account:

- four additional temperature-time curves validating the calorimeter's performance
- four additional temperature-time curves for determining the calorimeter's constant
- data tables for the data in each figure appearing in this report or the appendix

Appendix Two: Checklist for Formal Reports

Abstract – Does your abstract:

- □ state the purpose of experiment?
- □ summarize key experimental results?
- □ where possible, compare experimental results to theoretical results?

Introduction – Does your introduction:

- □ provide a context for the experiment, including appropriate references?
- □ clearly explain how your experiment fits within the broader context of the course's three main topics (i.e. thermodynamics, equilibria, and kinetics)?
- □ explain why the experimental approach used is suitable and briefly outline any relevant theory?[1]
- □ clearly state the goal(s) of your experiment

Procedure – Does your procedure:

- □ avoid reading as though it is a list or as a timeline?
- □ provide only essential details?
- □ omit numerical information that is not critical or that will be included with the results and conclusions?

Results and Conclusion – Are your results and conclusions:

- □ presented in a logically structured manner?
- □ supported by tables and figures, as appropriate?
- □ clearly stated and, where appropriate, compared to theoretical or expected results?
- □ supported by an analysis of reasonable experimental errors?

Miscellaneous – Have you:

- □ checked to see that information is not repeated in different sections of your report?
- □ discussed each table and figure in your report?
- □ carefully checked your spelling and grammar?
- □ ensured that there is enough information included in your report to verify your results and conclusions?
- □ paid attention to significant figures and units?
- □ properly referenced the work of others?

[1] Alternatively, the relevant theory may be developed in the results and conclusions section.

Figures – For each figure, did you:

- □ properly number the figure and include an informative caption?
- □ choose an appropriate scale for each axis?
- □ set the background area to white?
- □ remove gridlines unless they are critical to interpolating the data?
- □ properly labeled the axes (including units)?
- □ ensure that multiply data sets are easily and clearly identified? (note: do not include a legend if the figure contains only one data set)
- □ remove connecting lines between data points (unless such lines are critical to following trends when displaying multiple data sets)?
- □ (if necessary) ensure that your data points are not obscured by the inclusion of a regression line?

Tables – For each table, did you:

- □ properly number the table and include an informative title?
- □ include all relevant measurements and final results?
- □ exclude unnecessary information, such as intermediate calculations?
- □ properly labeled the rows and/or columns (including units)?
- □ use appropriate significant figures?

Appendix Three: Density of Water

Temperature, ^{o}C	Density, g/mL
15	0.9991026
16	0.9989460
17	0.9987779
18	0.9985986
19	0.9984082
20	0.9982071
21	0.9979955
22	0.9977735
23	0.9975415
24	0.9972995
25	0.9970479
26	0.9967867
27	0.9965162
28	0.9962365
29	0.9959478
30	0.9956502