

PHYSICAL CHEMISTRY LABORATORY



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Howard University
Howard: Physical Chemistry Laboratory

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TABLE OF CONTENTS

Licensing

1: New Page

- 1.1: Safety Laboratory Exercise
- 1.2: Chemical Literature
- 1.3: Experimental Error and Statistics
- 1.4: Chemical Conceptions and Misconceptions
- 1.5: Numerical Data Analysis
- 1.6: Computation of Thermodynamic Quantities
- 1.7: Equation of State
- 1.8: Heat Capacity Ratios for Gases (C_p/C_v)
- 1.9: Chemical Garden - Introduction to Research
- 1.10: Blackbody Radiation
- 1.11: Atomic Spectroscopy
- 1.12: UV-Vis Absorption Spectroscopy
- 1.13: Particle in a Box
- 1.14: Fourier Transform Infrared Spectroscopy (FTIR)
- 1.15: Biomaterials- Protein Structure Determination by FTIR Spectroscopy
- 1.16: Biomaterials- Studies of Protein Structure by Computational Quantum Chemistry
- 1.17: Nano-Particles and Quantum Dots
- 1.18: Kinetics of Hydrogen Peroxide Decomposition

Index

Glossary

Detailed Licensing

Licensing

A detailed breakdown of this resource's licensing can be found in [Back Matter/Detailed Licensing](#).

CHAPTER OVERVIEW

1: New Page

- 1.1: Safety Laboratory Exercise
- 1.2: Chemical Literature
- 1.3: Experimental Error and Statistics
- 1.4: Chemical Conceptions and Misconceptions
- 1.5: Numerical Data Analysis
- 1.6: Computation of Thermodynamic Quantities
- 1.7: Equation of State
- 1.8: Heat Capacity Ratios for Gases (C_p/C_v)
- 1.9: Chemical Garden - Introduction to Research
- 1.10: Blackbody Radiation
- 1.11: Atomic Spectroscopy
- 1.12: UV-Vis Absorption Spectroscopy
- 1.13: Particle in a Box
- 1.14: Fourier Transform Infrared Spectroscopy (FTIR)
- 1.15: Biomaterials- Protein Structure Determination by FTIR Spectroscopy
- 1.16: Biomaterials- Studies of Protein Structure by Computational Quantum Chemistry
- 1.17: Nano-Particles and Quantum Dots
- 1.18: Kinetics of Hydrogen Peroxide Decomposition

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1.1: Safety Laboratory Exercise

Exercise 1. Safety in the laboratory

Profs. Stockwell and Morris

August 2016

Purpose

Students will become aware of laboratory hazards, safety rules, safety equipment and responsibilities.

Report

The report for this exercise will consist of the following:

Your quizzes for each of the safety modules taken,

A paragraph on what you find in the Material Safety Data Sheet for Toluene,

A Material Safety Data Sheet for a compound of your choice,

A paragraph on what you find in the assigned Material Safety Data Sheet for the compound of your choice,

A 1-2 page summary on one of the examples of a safety disaster given below,

A map of the Physical Chemistry Laboratory and exterior hallway showing safety equipment and exits,

Core Safety Rules to be Followed at ALL TIMES

1. No one, including professors, should work in the laboratory alone.
2. Proper clothing must be worn.
3. Use the prescribed amounts of material. Do not waste.
4. Report broken equipment immediately.
5. No smoking in the laboratory.
6. No eating or drinking in the laboratory.
7. Eye protection - Safety goggles or eyeglasses must be worn at all times.
8. Reactions that produce toxic vapors must be carried out in the fume hood.
9. Wash with lots of water in the event of a strong acid or base burn.
10. Treat everyone with courtesy and respect.

More General Rules

Electrical Hazards

If you ever have to maintain an electrical apparatus or computer it should be unplugged from any power source. It is not safe to simply turn it off. If you must place electrical test probes in a solution use one hand to avoid any possibility of conducting an electric current through your heart.

Heating mantles, used to heat solutions, are to be plugged into the variable transformers and never directly into the power outlets.

Laser and Radiation Hazards

Do not look into the beam of a laser even if the beam has a very low power. Shiny watches and/or jewelry are not okay in a laser lab under any conditions because they may reflect stray radiation into someone's eyes. Certain types of UV lamps can damage eyes and produce a sunburn effect on the skin.

Vacuum and High Pressure

Special glass vessels without cracks or scratches, with thick walls, are preferred when constructing vacuum apparatus. They should be wrapped in tape to prevent glass from flying if the vessel implodes.

When you place a regulator onto a gas cylinder you want to secure it firmly but not so that you risk twisting the neck off the

cylinder. Whenever you turn it on you want to stand away from the direct line between the regulator and the cylinder in case the regulator was installed incorrectly and flies off the cylinder.

Procedure

Part 1:

Take the safety training course at: <http://labsafetyworkspace.org>

* The course list is at: <http://labsafetyworkspace.org/training-course-list>.

* Take the course: Introduction to Laboratory Safety.

* Print and attach your certificate of completion to your report.

* You will have to register but the course is free.

Part 2:

Find and describe Material Safety Data Sheets (MSDS).

Your best source of safety information on chemicals is a Material Safety Data Sheet (MSDS). The MSDS describes the properties of a laboratory or industrial chemical and chemical mixtures. It is concerned with safety and product stewardship. It is especially for workers and safety personnel. It gives important warnings and procedures for safe handling of the substance. The information may include melting and boiling points, hazards, toxicity, health effects, first aid and other useful things such as storage and disposal information. See:

There are many sources for MSDS. A list is at <http://ehs.okstate.edu/links/msds.htm>.

Click at the link marked MSDS Library (Air Liquide) <https://industry.airliquide.us/resources/safety-data-sheets>. You will come to a page marked "Click here to find the safety data sheet you need" and click here. That will give you a search box.

Enter the chemical in the search form and perform the search. Try searching for "Toluene" and be sure you click on the menu to set "Begins With". You will come to a page with a number of choices. Select the entry with just Toluene and write a paragraph describing the entry that you find.

Do a similar search on another chemical that you believe has some dangers. Write another paragraph describing the MSDA that you find for this chemical. Print the first page of this MSDS that you find and include it with your report.

Fill free to try the other sources of MSDS on the Oklahoma State University list.

Part 3:

Prepare a 1-2 page summary of one of the examples (the topics can be selected randomly) and they will be expected to discuss in detail next week. There are some fundamental chemical concepts in play with both of these types of the explosions and fires that are interesting to explore. The first is a very tragic example of why safety should be followed at all costs.

UCLA Chemist Fatality:

<http://www.rsc.org/chemistryworld/2013/05/ucla-chemist-trial-safety-violations-linked-sheri-sangji-death>

And

<http://cen.acs.org/articles/90/web/2012/01/Systemic-FailuresCited-UCLA-Lab-Fatality.html>

Propane plant in Florida:

<http://www.cnn.com/2013/07/30/us/florida-propane-explosion>

Fertilizer plant in Texas

<http://www.cnn.com/2013/06/27/us/texas-explosion/index.html>

Part 4:

Survey the Physical Chemistry Laboratory and the surrounding hall way for safety equipment.

Make a map on the attached worksheet. Identify the layout of the Physical Chemistry Laboratory and hallway outside in order to draw a map. On the map show the location of the following: fire blankets, fire extinguishers, fume hoods, spill kits, eye wash, safety shower and first-aid kits. There are containers in the lab to throw away all sharp objects, broken glass, and hazardous chemicals. Identify them on the map and use them. The chemical spill kits for acids, bases and solvents are in the hallway along with other fire extinguishers. List these on your map too.

FORM

Map of Howard University Physical Chemistry Laboratory with Surrounding Hallway.

Name: _____

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1.2: Chemical Literature

Using Scientific Literature

In this initial exercise you will learn more about searching the scientific literature. You need not follow the standard format for labs for your report (this applies to this report only). Next week's quiz will include material from this discussion.

Goal

The goal of scientific research is to produce new knowledge that others may use. Performing a literature search can save you much work and even embarrassment in the long run. Google, Wikipedia and other similar resources are very useful. However you need go beyond these for serious scientific research.

Why We Need Peer Review

This video presents an outstanding explanation of why media reports of science are often completely wrong. This is why we need the scientific peer review process.

Watch: Scientific Studies: Last Week Tonight with John Oliver (HBO)

<https://www.youtube.com/watch?v=0Rnq1NpHdmw>

Structure of a Typical Scientific Paper

- Although each scientific paper may be a little different, most papers follow the following template.
- Abstract
- Short Introduction describing the purpose, relevant theory and derived equations.
- Experimental with a short description of the apparatus and procedures.
- Results including sample calculations, tabulated results with error bounds.
- Conclusions with a discussion of error, precision and accuracy as appropriate. Compares results with any other available literature values and discusses error and accuracy.
- References. A citation of all sources including books, peer reviewed journals and the internet.

Peer Reviewed Scientific Journals

Peer reviewed scientific journals remain the most important source of information for scientists. Examples include the New England Journal of Medicine, Nature, Science, the Journal of the American Chemical Society. Peer review refers to the process where papers are submitted to journals. The papers are sent anonymously to other scientists who review the papers for importance, errors, length, readability and other things. Reviewers make recommendation to editors who reject or accept them depending upon the reviews. Peer review is the "gold standard" of the scientific process although mistakes are often made. It does not guarantee that the paper is correct but it catches obvious errors and fraud (usually)

Other Primary Sources

Preprints (papers sent to journals and under peer review are now often available before their acceptance by journals but beware! Some many never appear due to errors found during peer review.

The "Gray Literature"

- Masters and Ph.D. Dissertations
- Government Reports
- Proceedings from scientific meetings
- Patents

Secondary Literature

The secondary literature presents results that are compiled from the primary sources. Textbooks are a form of secondary literature with which you are probably most familiar. Other important sources include indexes and abstracts. These include sources such as

Chemical Abstracts, Medline and Web of Science. Other excellent sources include review journals such as Chemical Reviews and Reviews of Geophysics; and data collections such as the CRC Handbook.

Chemical Abstracts and SciFinder Scholar

Chemical abstracts is the most respected source of chemical information and guide to the literature. The print version began in 1907 and the electronic version began in 1967. It covers almost anything in the primary literature that can be construed to be new research in chemistry or chemical engineering. This means that it also includes much about the literature in biology, environment, geology, materials, medicine and physics. Coverage is global and it tries to include all languages. You can search it in many ways including by keywords, title and authors. SciFinder Scholar is an electronic version of chemical abstracts.

MEDLINE® (Medical Literature Analysis and Retrieval System Online)

MEDLINE is a leading bibliographic database for medicine, medicinal chemistry and the life sciences. Given the importance of chemistry for medicine, MEDLINE includes a significant amount of abstracts in most areas of chemistry. An advantage of MEDLINE is that it's free and available to the general public. MEDLINE contains citations of over 15 million journal articles. It begins in about 1950 (there is some older material) to the present. There are citations from approximately 5,000 journals in 37 languages. MEDLINE is a subset of PubMed® which is, in turn, one of the databases provided by US National Library of Medicine's National Center for Biotechnology Information (Source US National Library of Medicine website; see below).

Instructions for MEDLINE®

1) MEDLINE: Go to the US National Library of Medicine (National Institutes of Health) website:

<http://www.nlm.nih.gov/>

2) Go to PubMed in upper left-hand corner.

3) Try an author search first. Type a name of one of our faculty in the search box at the top and submit. If no articles appear try again. If too many appear try a list of two names or more. Now you will find fewer citations. For example suppose that you are looking for a paper written by Fujita AND Stockwell. Arrive at a more reasonable number of abstracts. View one of the abstracts by clicking on its title.

4) Now try a subject search. It works just like the author search.

Google Scholar

A Google search engine focused on the scholarly literature. Works mostly like Google; see the site at: <http://scholar.google.com/>

American Chemical Society

To see a list of journals published by the ACS go to: <http://pubs.acs.org/action/showPublications?display=journals>

Search these journals at: <http://portal.acs.org/portal/acs/corg/content>

Science - American Association for the Advancement of Science

<http://www.sciencemag.org/>

Beware of Science Fraud

Approximately one published scientific paper per day is retracted due to some form of misconduct that ranges from plagiarism to fabricating results. Two percent of scientists say they have fudged their data in publications. Do not commit fraud in your laboratory reports or during your professional career.

Read: What's Behind Big Science Frauds?

By Adam Marcus and Ivan Oransky May 22, 2015 in the New York Times.

http://www.nytimes.com/2015/05/23/opinion/whats-behind-big-science-frauds.html?_r=0

Assignment - To Do

In this initial exercise you will perform a literature search by using an online abstract service. Most operate in more or less the same way. Given the health profession orientation of many in our class you can use MEDLINE® OR the other sites listed above.

Complete Table 1

Complete Table 1 using MEDLINE to perform the search, or use or another one of the databases listed above. Be sure to put you name and the database you used and write down how many citations you find for your search.

Name _____ Database _____

Table 1. Subject / Keyword Search Results – The quotes are necessary where shown.

Search Term	Number of Citations
Thermodynamics	
"Quantum Mechanics"	
Enzyme	
Protein	
Thermodynamics AND Enzyme	
"Quantum mechanics" AND Enzyme	
Kinetics	
Kinetics AND Enzyme	
Kinetics AND Thermodynamics	
Spectroscopy	
Spectroscopy AND Enzyme	
"X-Ray Crystallography"	
Hydrogen Peroxide	
H2O2	

Discuss the Results for Table 1.

Notice that many of the searches in Table 1 are linked, such as the search for Enzyme and the search for Thermodynamics AND Enzyme. Write a paragraph that discusses the differences between the connected search terms. Include in your report.

Find a Paper by Using a Search Strategy

The best databases include links so that you can download papers. However costs are usually involved. Howard University has several subscriptions that are free to you when used within the university. Come up with a total of three search terms. These may be authors or key words or some combination of these and list in the Report section. Use the search terms to find a recent research article in a primary peer reviewed journal. You may need to revise the search terms depending on your results. Try to find a paper that includes all or most of the standard paper components that we discussed in class (Abstract, Experimental (or methods), Results, Discussion and References). Do not worry if the paper does not contain an Appendix because its not included in the typical paper. Download the paper to your computer.

Each student will find a unique paper. You must use a defensible search strategy; just using a paper that you happen to have does not count.

After you find a paper, **Reserve It** by writing down its reference on the reservation sheet on my door.

Write a Paragraph Explaining Your Search Strategy

To get credit for this part you must successfully explain in your report how you found your paper from the databases. From your report I need to be able to find it from your description.

Include in your discussion a list of your search terms such as:

Term 1. Thermodynamics; Term 2. Kinetics; Term 3. Enzyme

Discuss the Paper Briefly

For the primary research paper that you found discuss its format. How well does it present its results? I am not looking for a detailed review, just a short assessment that should be expressed in two or three paragraphs. If you were the reviewer would you recommend major changes (why or why not)?

More Questions to Answer in Your Report

1. What is the difference between the primary and secondary scientific literature?
2. Discuss the differences between a paper in a peer-reviewed journal, a review article and a textbook.
3. Given the same paper, would scientists believe it more if it were published in Nature or a Federal Government Report? Why?
4. Discuss the peer review process. What are its virtues? Can you imagine any serious problems and deficiencies?
5. Suppose you are new to a specialized research area but familiar with the overall subject. Would it be better to begin your search with a paper in a peer reviewed journal, a review article or a textbook? Defend your answer.
6. Compare the Example Databases to Google and the Wikipedia. What are their relative strengths and weaknesses?

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1.3: Experimental Error and Statistics

Density, Experimental Error and Data Analysis

Purpose

The purpose of this laboratory is to collect datasets that will be used to show the random and systematic errors associated with any measurement. The student will learn about data analysis. Density measurements will be used as the first example. Density is chosen because it is a familiar concept and this allows the student to focus on the new concepts of experimental error in this laboratory.

Introduction

Density, and extensive and intensive properties

Mass and volume are extensive properties. Extensive properties depend on the amount of substance present in a sample. Usually an intensive property results if two extensive properties are divided. An intensive property is a characteristic of a substance and does not depend on the amount present.

Density (d) is an example of an intensive property derived from two extensive properties, mass (m) and volume (V).

$$d = \frac{m}{V}$$

Although there are many ways to measure density for specialized applications, in this laboratory we will measure density by measuring the mass and volumes of samples and then calculating the density.

Experimental Error

No measurement is perfectly exact and in fact all measurements have random errors systematic errors. Suppose that the same measurement was repeated a large number of times. Random error prevents the measurement from giving you the same value every time. Figure 1 is a distribution that shows the general result for a repeated measurement. The x-axis shows the measured values as the experiment was repeated. The y-axis shows the number of times the experiment yielded a particular measured value.

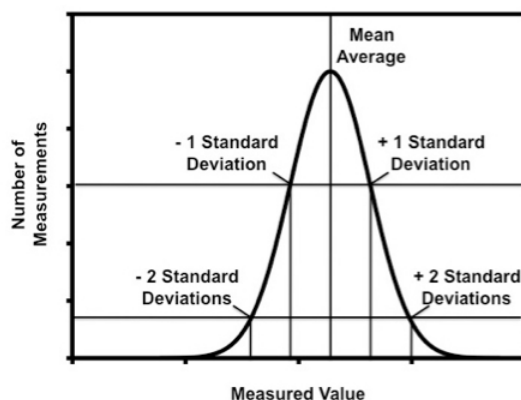


Figure 1. An experiment was repeated many times. The measured values are plotted on the x-axis and the number of times a given value was measured is plotted on the y-axis. The standard deviation is .

Random error leads to the Gaussian (or normal distribution) shown in Figure 1. The mean average is the most frequently measured value. The mean, $\bar{x}$, is given by:

$$\bar{x} = \frac{\sum x_i}{N}$$

where: x_i are the measured values and N is the total number of measurements. The standard deviation of the mean, σ , is given by:

$$\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N - 1}}$$

An apparatus or a procedure for a measurement may have systematic errors. The difference between random and systematic error is that systematic errors can lead to bias whereas random errors contribute to imprecision. For example the measurement may have a bias that tends to yield higher or lower values than the “true” value, Figure 2.

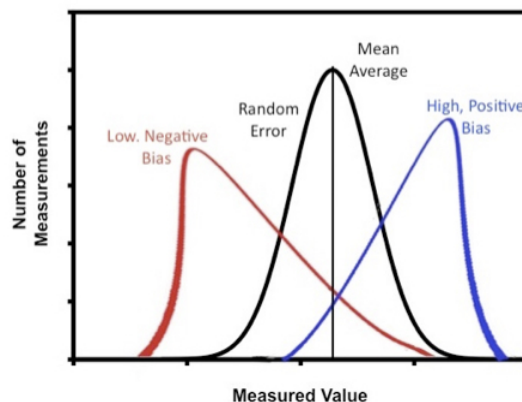


Figure 2: An experiment was repeated many times. The distribution in red shows low or negative bias. The distribution in blue shows high or negative bias. The curve in black is the normal distribution due to random error. The mean average or “true” value is marked on the normal distribution.

Systematic errors may be fixed (e.g. constant in magnitude) or proportional in magnitude to concentration or other experimental variables. Since the averaging of a very large number of replicate measurements will reduce the random error, the total error for a system of measurements will tend towards the systematic error as the number of replicate measurements increases. You may be able to test this result based on a comparison of all data generated by the class.

Experimental Procedure

You will measure the volume and mass of three substances that were chosen to be somewhat difficult. Your grade does not depend on getting the “right” density but it does depend on your learning about measurements. The substances are navy beans, Styrofoam and ice.

1) Navy Beans: Each group will take a clean and dry 250 ml beaker, weigh it on a top-loading balance and record its mass. Remove the beaker from the balance and then weigh it again. Weigh the beaker a total of 5 times. Ask yourself if you always get the same results.

Add 50 ml of beans to the beaker, weigh it and record the total mass. Pour out the beans back to the stock of beans and stir the stock of beans so that you will not be weighing all the same beans again. Measure another 50 ml of beans and weigh. Do not try to get the same mass as the first by adding, subtracting, shaking the beaker... doing these kinds of things introduces systematic bias and will ruin the experiments. Repeat this procedure for a total of 10 times.

Repeat for 100 ml of beans. Repeat this for a total of 10 times with volumes of 100 ml of beans.

Repeat for 150 ml of beans. Repeat this for a total of 10 times with volumes of 150 ml of beans.

Repeat for 200 ml of beans. Repeat this for a total of 10 times with volumes of 200 ml of beans.

2) Styrofoam: Repeat the procedure above but substitute Styrofoam for the navy beans.

3) Ice: Repeat the procedure above but substitute ice for the navy beans. Make sure that you use a paper towel to dry the ice before weighing it and do not handle it with your fingers (Why not?). This is difficult but do the best you can to remove the water. You may find that there is some systematic bias in the ice measurements. Describe the sources and types of error in your lab report.

4) Data Pooling: We will pool our data across all groups and be sure to submit your data to the instructors at the end of the lab period.

Data Analysis – Error and Distributions

The data will be provided in an Excel spreadsheet and you will calculate the density of the beans, Styrofoam and ice from the measurements. Keep four significant digits in these calculations.

Calculate the average mass of the beaker. The mean average, $\bar{x}$, is given by:

$$\bar{x} = \frac{\sum x_i}{N}$$

where: x_i are the measured values and N is the total number of measurements. Determine the standard deviation of the mass measurements for the empty beaker with the formula,

$$\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N - 1}}$$

Calculate the density for all of the mass measurements from the following formula,

$$d = \frac{m_i - m_b}{V}$$

where m_i is the measured total mass, m_b is the mass of the empty beaker and V is the volume (50, 100, 150 and 200 ml). For the mass of the beaker use its average mass. You will get a set of densities for navy beans, Styrofoam and ice. For example a sample dataset for navy beans is given below.

Table 1: Volume and mass measurements, and calculated densities for navy beans.

Volume (ml)	Mass (g)	Density (g / ml)	Volume (ml)	Mass (g)	Density (g / ml)
0.000	114.0				
50.00	154.0	0.800	150.0	248.0	0.893
50.00	154.2	0.804	150.0	242.2	0.855
50.00	160.2	0.924	150.0	239.2	0.835
50.00	158.2	0.884	150.0	248.2	0.895
50.00	158.0	0.880	150.0	242.3	0.855
50.00	152.1	0.762	150.0	240.5	0.843
100.0	197.0	0.830	200.0	276.8	0.814
100.0	204.2	0.902	200.0	280.4	0.832
100.0	199.8	0.858	200.0	282.0	0.840
100.0	195.9	0.819	200.0	282.2	0.841
100.0	201.5	0.875	200.0	283.8	0.849
100.0	203.1	0.891	200.0	279.2	0.826

Calculate the mean average and the standard deviation for the densities of the beans, Styrofoam and ice. For example, the average and the standard deviation of the limited dataset above are 0.85 g/ml and 0.038 g/ml, respectively.

Next take the density for each substance and sort it (there is an Excel command for this). Below is an example from the sample dataset.

Table 2: The calculated densities for navy beans are arranged from low to high values.

Density (g / ml)	Density (g / ml)
0.762	0.849
0.800	0.855
0.804	0.855
0.814	0.858
0.819	0.875
0.826	0.880
0.830	0.884
0.832	0.891
0.835	0.893
0.840	0.895
0.841	0.902
0.843	0.924

This is the same data as above. The data as been sorted from low to high values.

Sort the data into bins consisting of equal data ranges. See the example below. You will have to adjust the size range of the bin to get a good understanding of the distribution. Describe the thought process used to determine your bin sizes. WARNING: We do NOT expect that everyone thinks the exact same way.

Table 3. The calculated densities for navy beans sorted into bins consisting of a range 0.03 g/ml per bin.

Density Range (g / ml)	Number of Values in the Range
<0.799	1
0.80-0.8299	5
0.83-0.8599	10
0.86-0.8899	3
0.89-0.9199	4
>0.92	1

Make a plot of the density range and the number of values similar to Figure 3 for each substance. Fit a polynomial curve to the bars to see the distribution better.

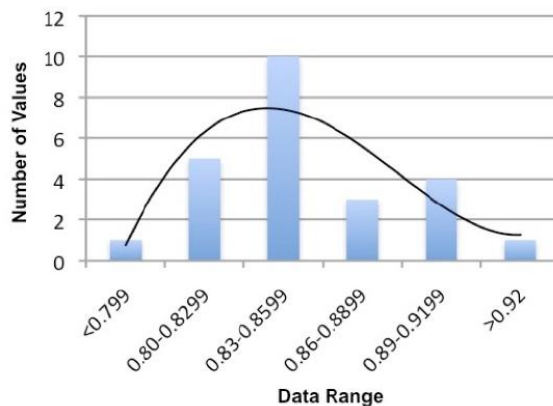


Figure 3. A plot of the distribution derived from Table 3. Note that it is not too far from the normal distribution. There may be a small systematic negative bias in the measurements.

Data Analysis – Part 2 – Analysis by Linear Regression

Read the handout “Error, Accuracy, Precision and Linear Regression”. There is another method to treat the measurements that usually results in more accurate results. This method is linear regression.

An Excel spreadsheet for linear regression is supplied. An advantage of the spreadsheet is that it gives the best fit slope, intercept and their standard deviations. The standard deviations are not available from the standard version of Excel, you have to buy an extra Excel statistical package to have them.

Make three copies of the original spreadsheet for linear regression and save the original in case you mess up one of the copies. Paste all of the volume and mass measurements for each substance into a copy of the Excel spreadsheet. Include values made with the empty beaker and enter the volume as zero for these.

Copy the regression plots along with the best fit slope, intercept and their standard deviations into your laboratory report. You should add labels to the axes of the plots, Figure 4. The slope is the density for each substance and the standard deviation of the slope is the standard deviation of the density. Compare the values calculated by linear regression with the results from Part 1. Is the standard deviation of the density larger or smaller than the one calculated in Part 1?

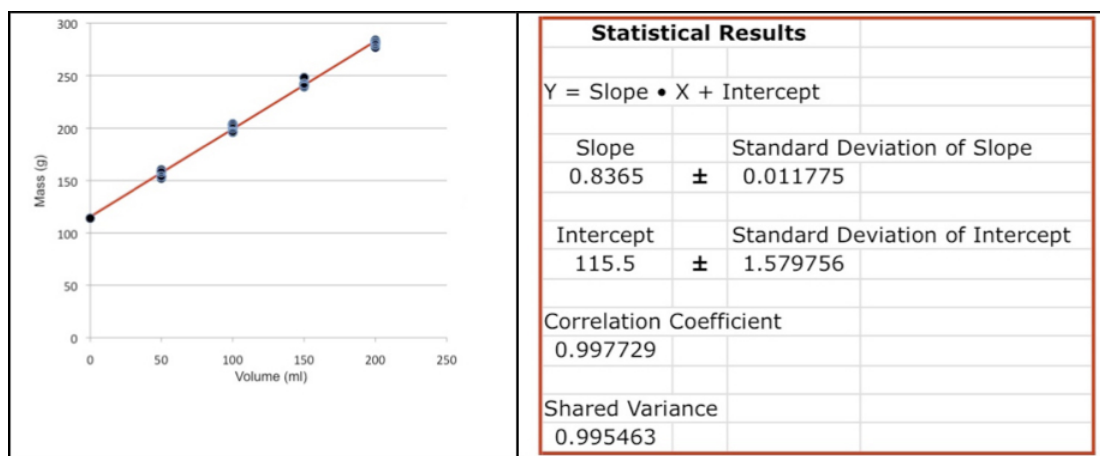


Figure 4: A plot of the linear regression of all data from Table 1 showing the best-fit line. The statistical results from the spreadsheet for linear regression are shown on the right.

Purpose

In this laboratory you will learn the general theory of calibration. To perform the calibrations you need to understand the concepts of significant figures, measurement error, accuracy, precision, propagation of errors, graphing and linear regression.

Introduction

It is easy to buy any number of measuring devices: thermometers, scales to measure your weight, watches and timers, laboratory instruments etc. To often, at least at home, people just trust the numbers coming out of the measuring devices. Chemists make measurements with some devices that they have used for centuries, such as volumetric glassware (pipettes, graduated cylinders, etc.) and chemical balances and with modern spectrometers. In a medical laboratory or in a hospital the results may be disastrous if the numbers are not accurate. How do can you know that the measurements correspond to reality? Calibration of the measurement device is required. **Calibration is the process that correlates an instrument's response with known standards.** In this laboratory you will perform a calibrations of a UV-Vis spectrometer.

Calibration of a UV-Visible Spectrometer

1. First you will use an Ocean Optics visible spectrometer and a hydrogen discharge lamp. Turn on the hydrogen lamp and examine its spectrum. Use the green cursor to read the wavelengths of the hydrogen lines.
 - One of the spectra should be read at a low enough integration time so that none of the lines “peak out”.
 - The second spectra should be recorded at a higher integration time so that you can see lines with lower intensity.
 - Each group will make their own spectral measurements.
2. Repeat this procedure for argon and mercury **using the same spectrometer that you used for your group's hydrogen spectra.**
3. Make one calibration curve for your spectrometer using your data that includes both your hydrogen and argon data.

Make a table in Excel with your wavelengths measured lines and the known lines. Note that there will be differences between the wavelengths of the peaks as measured by the spectrometer and their known wavelengths. For hydrogen the known lines are 656.3, 486.1, 434.1 and 410.2 nm. You can check these spectral lines and find the ones for argon at: <http://physics.nist.gov/PhysRefData/ASD/index.html>. Note that H I and Ar I are the atoms of H and Ar, respectively.

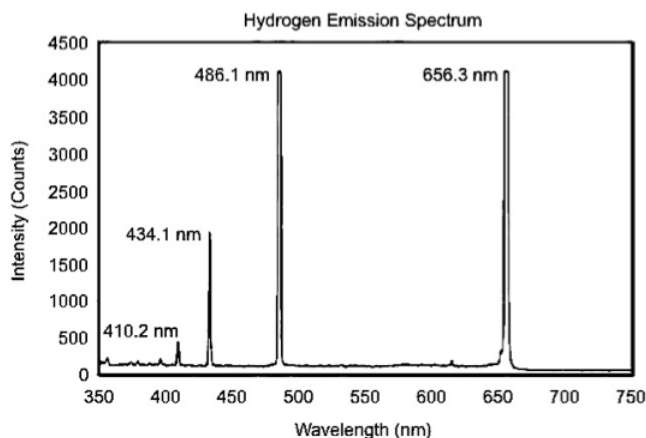


Figure 5: A plot of the known emission lines for hydrogen.

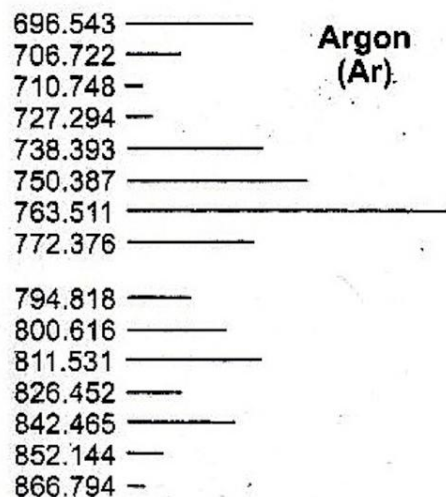


Figure 6: A plot of the known emission lines for argon.

4. Plot the points and determine slope and intercept as you have done in the previous sections. It is strongly suggested that you use the known lines as the “y-axis” and your measured lines as the “x-axis”.
5. Copy the hydrogen lines into the Linear Regression Spreadsheet and calculate the slope, standard deviation of slope, intercept, standard deviation of intercept, the correlation coefficient and the shared variance for these data. The equation that you will get is the following:

$$\text{Calibrated Wavelengths} = \text{slope} * \text{measure wavelength} + \text{intercept}$$

6. Copy the statistical results and the plot of the calibration curve for the wavelength scale into your laboratory report in the Results section.

See Also: <http://www.astronomyknowhow.com/hydrogen-alpha.htm>

Report

You may combine this section with the first part on density to create one report. Comment on the bias of all the measurements.

The Linear Regression Spreadsheet is Available at:

[Linear_Regression.xls](#)

A weighted least squares regression spreadsheet is available at:

[Linear_Regression_Weighted.xls](#)

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1.4: Chemical Conceptions and Misconceptions

Chemical Conceptions and Misconceptions

Prof. V. Morris

Purpose

In this initial laboratory exercise you will shake the rust off of your laboratory investigative skills by using some basic tools of logic and your background knowledge of chemistry to distinguish and classify several unknown solids based on their physical chemical properties. The format of this laboratory report will vary slightly from the standard format for labs because of its open-ended nature. Quite often the need to think independently, to make rational choices based on common observation is frightening to students. This is especially the case when most of your courses have only required you to apply some memorized process. This purpose of this lab is to get your creative juices flowing and additionally promoting nascent knowledge recall and usage.

I. Observations of Thermodynamic Processes

Objectives:

To engage students in applying observational skills and to relate these observations of common physical processes to Thermodynamics lecture topics in Physical Chemistry. This exercise will also examine individual student conceptions (and misconceptions) of diffusion, the zeroth and first laws of thermodynamics, and entropy.

Several solutions of varying composition and temperature will be mixed. You should predict the results of the experiments, carefully observe the demonstrations, observe the results, and interpret them using appropriate thermodynamic terms. Every attempt should be made to relate what you see to the laws of thermodynamics, state variables and state functions, equilibrium, and energy transfer.

Procedure:

1. Observe and record the chemical and physical properties of the solutions that will be used in this demonstration.
2. Between two and six individual experiments will be conducted. For each experiment, predict what will happen and provide a justification.
3. Carefully observe each experiment and compare your prediction to the eventual result. Was your prediction correct? Was your justification sound?
4. What misconceptions can you identify in your original thinking?
5. Which misconceptions (if any) do you think were addressed by this exercise?

Elements to address in your report

1. What thermodynamic principles determined the behavior of the solutions being mixed in these demonstrations?
2. Briefly explain the results of each demonstration
3. How does the first law of thermodynamics apply?
4. Which state variables were changed during the demonstrations?
5. For each incorrect prediction, explain the misconception.

II. Physical Chemical Discrimination

Objective: Use your chemical intuition, your knowledge, and the resources provided in this lab to identify and discriminate the chemical and physical properties of four granular solids. In particular, you need to determine:

- a. Whether the solid is a compound or a mixture
- b. The nature of the bonding in the solid
- c. Your best guess at chemical composition (e.g. an organic acid, an inorganic salt, a plastic)
- d. At least three other chemical or physical properties (preferably thermodynamic)
- e. Explain whether the properties that you determine are extensive or intensive.

The common substances are some combination of the following that covers metallic bonded, covalently bonded, ionically bonded, inorganic and inorganic materials as well as mixtures and pure materials.

Procedure:

1. The class will be divided into groups of three or four students. Each group will work together to develop a single lab report to submit. All members of the group must sign off on the cover page of the lab report.
2. Each group will be assigned a suite of four granular solids indicated only by a number between 1 and 9.
3. Physically examine each of your solids and make an exhaustive list of your observations. Try to determine specific physical properties of the substance. What distinguishes it from the other solids? This should be reported in your report as a table. An example is given below.

SAMPLE OBSERVATIONS TABLE

Sample Number	General Observations	Initial Predictions for Solvent Interactions	Results of Solvent Interactions	Initial Predictions of Physical Methods	Results of Physical Methods
7	Bluish color with brown specks, smells pungent, begins to glow eerily after a few minutes	The sample will explode upon contact with water	The sample exploded upon contact with water	The sample will create an acidic aqueous solution	The sample created a basic aqueous solution

4. Based on your physical examination and observations predict the type of bonding in each solid (e.g. ionic, covalent, polar covalent, non-polar covalent, metallic). You will attempt to test these guesses in subsequent steps.
5. Examine the two carts at the front of the lab. One cart has some standard instrumentation and devices and the other contains a suite of common solvents. Based on your observations and discussions within your group, identify two solvents to use to determine further chemical and physical properties.
6. Obtain small volumes of the solvents (usually less than 25-ml) and bring back to the bench to sequentially test for chemical and or physical properties of each solid. Do NOT mix the solvents.
7. Add small amounts of your first solvent dropwise to a small amount of each sample (individually). You may use either a watch glass or a small beaker for this part. Continue until there is no further chemical change, physical change, or complete dissolution. Record your observations.
8. Repeat this procedure for the other solvent and fresh amounts of your samples.
9. Return to your initial guesses. How consistent are they with respect to this new information?
10. Return to the carts and review the contents of the hardware table. Select no more than two devices to use to determine additional chemical or physical properties. Record your observations.
11. Dispose of the chemical materials (Ask the instructor), clean all glassware, and clean bench area

Elements to address in your report

1. Which two solvents did you select and why?
2. What did you learn about each of your solids using the solvents?
3. Link your observations to the identification of physical properties
4. Which two devices did you select and why?
5. What did you learn about each of your solids using the devices?
6. What is the identity of each of your solids?
7. If you had a choice to select one additional solvent or one additional instrument to assist in your determination, what would it be and why?
8. If you had a choice to select one additional solvent or one additional instrument not present on the carts to assist in your determination, what would it be and why?

9. Design and present a data table that illustrates and compares what you “know” about each substance based on the chemical and physical evidence and measurements. Imagine that you were part of a forensics competition and need to present your results to a panel of judges. The table should clearly represent your new state of knowledge.

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1.5: Numerical Data Analysis

Physical Chemistry Laboratory Fall 2016

Numerical Data Analysis

Professor Vernon Morris

Numerical analysis involves the practical use of mathematical calculations. Much like the Babylonian approximation of $\sqrt{2}$ (which turned out to have tremendous practical applications), modern numerical analysis does not seek exact answers, because exact answers are often impossible to obtain in practice. The current “arguments” revolving around “Climate Science” are a great example of this. The naysayers tend to focus on the existence of uncertainty as a reason to doubt everything. In fact, the constraints on the uncertainty are precisely why we should be paying great heed! Numerical analysis is concerned with obtaining approximate solutions while maintaining reasonable – as accurately as possible – bounds on errors.

Numerical analysis naturally finds applications throughout engineering and the physical sciences. The current century finds that life sciences, social sciences, and the arts have adopted various elements of numerical analysis and statistics as fundamental to their practice.

The overall goal of the field of numerical analysis is the design and quantitative study of techniques to give approximate but accurate solutions to hard problems, the variety of which is suggested by the following:

- Advanced numerical methods are essential in making highly accurate numerical weather prediction commonplace. (Consider the availability and specificity of the upcoming winter and seasonal forecasts compared to when you were in grade school.)
- Computing the trajectory of a spacecraft requires the accurate numerical solution of a system of ordinary differential equations. Recently, a rocket was not just launched but landed in vertical position. Others have been retrieved a sea on ships.
- Car companies can improve the crash safety and autonomous operations of their vehicles by using computer simulations. Such simulations essentially consist of solving partial differential equations numerically.
- Hedge funds (private investment funds) use tools from all fields of numerical analysis to attempt to calculate the value of stocks and derivatives more precisely than other market participants. (Google “Voodoo” economics sometime!)
- Airlines use sophisticated optimization algorithms to decide ticket prices, airplane and crew assignments and fuel needs. Historically, such algorithms were developed within the overlapping field of operations research.
- Insurance companies use numerical programs for actuarial analysis.

Purpose

The purpose of this assignment is to provide you with some experience exploring and analyzing data numerically, i.e. without using an information visualization system. You will be provided a data set (that can be imported into Excel) about the ambient atmosphere. You should explore and analyze this data using Excel or any other graphing or visualization tools with which you are familiar (e.g. Mathematica, MATLAB, S-Plus). Your goal here is to perform an exploratory analysis of the data set, to better understand the data set and its characteristics, and to develop insights about the environmental data.

Report

The report that you turn in should consist of five things.

1. First, list (bullet list of items) five “insights”, chunks of knowledge, or deeper questions that you either encountered or gained while exploring the data. An insight could be some understanding of the data and its characteristics that is not relatively obvious or intuitive. It is something that most people might not realize initially. Note that an insight or knowledge chunk simply may be a deeper question that arose in your mind while exploring the data and your cursory analysis may not have been sufficient to answer the question.
2. Plot the time series of the key environmental variable(s) supplied to you by the instructor. Based on your visual inspection, describe the temporal behaviors of each parameter and their apparent relationships to each other.
3. Perform and report on the outcomes of the following statistical techniques

- a. Determine the median and geometric means of each environmental parameter for all daytime hours, all nighttime hours, for the average day (24 hours) and over the entire observational period. Compute and report the average deviation and variance for each statistical measure.
 - b. Pick out the two groups (e.g. daytime, nighttime, full day, full observational period, or another descriptive measure of the data set) whose means are closest to each other. Do a two-sample t-test on the two groups you picked, using the Excel function described on the t-test page. Report the P-value and propose a plausible explanation what it means.
 - c. Do a two-sample t-test on the two groups in your data set with means that are the furthest apart. Report the P-value and propose a plausible explanation for what it means.
 - d. Perform a Pearson Correlation for all pairs of time-dependent variables from the data set. Report the R-values and propose a plausible explanation for what it indicates.
4. Attempt to “fit” the data with a mathematical function (e.g. linear, 2nd-degree polynomial, 3rd-degree polynomial). Which functions worked the best and for which parameters? What do you think is the purpose of such an exercise? What advice would you give someone who needs to fit a similar data set?
 5. Write two paragraphs about challenges or problems that you encountered in doing the analysis this way. Did anything limit or frustrate you? If nothing did, perhaps there was something that was more difficult than you thought it should be. Nothing is perfect, so you should be able to list some potential issues here.

[Down Load Data for Analysis Here](#)

[3_AirConc_200507.xls](#)

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1.6: Computation of Thermodynamic Quantities

Computation of Thermodynamic Quantities Based on Molecular Structure Calculations

Introduction:

The thermochemistry of common substances is largely known through carefully measured experiment. Thermochemical data for substances are available in data tables in both written and digital formats (e.g. Chemical and Engineering Data Reference Tables, CRC Handbook). Knowledge of the standard values of state functions such as the heat of formation, heat capacity, molar entropy, and free energy are useful in determining appropriate reaction conditions. This laboratory assignment is designed to provide a basic introduction to modern methods of computational thermochemistry, to thermochemical data, and to a comparison of the accuracy of computed values to experimental data. Note that this laboratory can be done in shifts, since there are only three machines with Spartan loaded in the PChem lab.

Objectives:

1. Learn to use computational chemistry software to optimize geometries and to model molecular behavior.
2. Perform computations of thermodynamic functions using equipartition theory and compare to literature values.
3. Evaluate the performance of various theoretical models used in computational chemistry with regards to thermochemistry

Procedure:

(Equipment Required: Computer with Spartan)

For this lab, you will compute IR vibrational frequencies and thermodynamic state function values for different molecules using several theoretical techniques. You will then compare the results to literature values for ideal and real gases as well as compare the performance of different theoretical models.

Running Spartan for Thermochemical Calculations.

1. Make a new file.
2. Build molecule by selecting atoms and clicking on screen.
3. Go to Setup Calculations, Select "Single Point Energy", depending on your case: molecular mechanics, semi-empirical, and Hartree-Fock (HF/3-21G), check IR and thermodynamics. You need not change anything else.
4. Go to submit and "submit".
5. Use Monitor to see if model is executing. (Should be very fast so might not be necessary).
6. Go to display and record thermodynamic values. Record the "contributions" to enthalpy, entropy, Cv ... Note that Total Enthalpy = Total vibration + ideal gas + translation + rotation.
7. Go to display spectra and write down the vibrational frequencies.

Computational Thermochemistry Simulations

1. Build and minimize molecular models for CH₂O, HCN, CO₂ and CH₄ using molecular mechanics, semi-empirical, and Hartree-Fock (HF/3-21G*).
2. Tabulate the thermochemical data for each simulation.
3. Tabulate the vibrational (IR) data for each simulation.
4. Perform a literature search to identify the thermodynamic constants and the vibrational frequencies of each molecule. Evaluate the % error, bias, and average absolute error for the thermodynamic constants and separately for the vibrational bands from literature values.
5. Compare and discuss the differences between the calculated thermodynamic values for the enthalpy, entropy and molar heat capacity and their corresponding literature values for each molecule. [You should construct a simple table of values]
6. Discuss the trends that you observe. For example, what was the trend in the %error for each constant as a function of computational method? What about the other statistical measures?
7. Compare and discuss the differences between the calculated thermodynamic values for the vibrational frequencies for each molecule. [You should construct a simple table of values here as well] Discuss the trends that you observe. For example, what

was the trend in errors for each constant as a function of computational method? How did the errors vary by molecular size? How did the errors vary as a function of vibrational mode?

8. Compute the vibrational contributions to the molar heat capacities of hydrogen cyanide and methane using a) the computed values of the vibrational frequencies and b) the literature values of the vibrational frequencies. To what do you attribute the differences in these quantities? Represent your data in tabulated form. Explain the trends and discuss the results. HINT: Use the vibrational temperatures for each gas to compute the molar heat capacities and note that the total vibrational heat capacity is equal to the sum of the heat capacities for the individual vibrational degrees of freedom.

The vibrational temperature, Θ_{vib} , is defined by the equation:

$$\Theta_{vib} = \frac{h\nu}{k}$$

where h is Planck's constant, c is the speed of light, ν is the frequency and k is Boltzmann's constant.

The vibrational contribution to the molar heat capacity from a given vibrational degree of freedom of frequency ν is given by:

$$(C_v)_{vib} = N \times R \times \left(\frac{\Theta_{vib}}{T} \right)^2 \times \frac{\exp(\Theta_{vib}/T)}{\{\exp(\Theta_{vib}/T) - 1\}^2}$$

where N is the number of moles, R is the ideal gas constant and T is temperature.

The total contribution to the heat capacity at constant volume from all vibrational degrees of freedom is:

$$C_{vib,Total} = \sum (C_v)_{vib}$$

where the summation is over all vibrational degrees of freedom, $3N-5$ (linear molecules) or $3N-6$ (non-linear molecules)

9. The speed of sound in any gas can be computed from the expression:

$$v_{sound} = \left\{ \left(\frac{C_p}{C_v} \right) \times \frac{RT}{M} \right\}^{1/2}$$

Where C_p is the heat capacity at constant pressure, C_v is the heat capacity at constant volume and M is the molecular mass of the gas. Use your computed values of molar C_v and C_p to derive a theoretical speed of sound for each of your gases and compare to each other and to their literature values. Evaluate the %error, bias, and average absolute error for the theoretical and "literature-derived" molar heat capacities. What trends, if any, do you observe both amongst the four gases (within a particular theoretical framework) and between individual gases computed across the framework. For the "literature-derived" sound velocities, use the tabulated values of the molar C_p and C_v at the standard temperature and pressure values of 298 K and 1 atmosphere.

To Calculate and Display the Distribution of Electrons

1. Setup the molecules as above.
2. Make a new file.
3. Build molecule by selecting atoms and clicking on screen.
4. Go to Setup Calculations, Select "Single Point Energy", and Hartree-Fock (HF/3-21G), check IR and thermodynamics. You need not change anything else.
5. Here you only need to run the Hartree-Fock (HF/3-21G),
6. Go into "Setup" menu and choose "Surfaces"
7. Click "Add" and choose Surface = density; property = Potential; click "OK"; close window.
8. Go to submit and "submit".
9. Use Monitor to see if model is executing. (Should be very fast so might not be necessary).
10. When completed go to "Results" menu and choose "Surfaces"; click on the box and see the potential surface around your molecule.
11. The red regions of the surface indicate the more electronegative regions of the molecule while the blue regions indicate the lower electronegative regions.

To Display the Vibrational Modes

12. Go to “Results” menu and choose IR. Check the box to display the entire spectrum. Click on the boxes to see the molecule vibrate in each of its modes.

Computational Thermochemistry Exercises Inorganic Molecules.

1. Build H_2 and run.
2. Build HCl and run.
3. Build HF and run.
4. Compare the electron distribution for these three molecules. What does this say about electronegativity?
5. Examine the vibrations for the three molecules and compare. Which molecule has the greatest vibrational frequency? Is there any relationship to the electronegativity?

Organic Molecules

1. Build benzene and run.
2. Build chlorobenzene and run.
3. Build toluene and run.
4. Build $\text{C}_6\text{H}_5\text{-O-CH}_3$ and run.
5. Compare the electron distribution for these three molecules. What does this say about electronegativity and the ability of groups to extract or donate charge to the ring?
6. Examine the vibrations for the four molecules and compare. Is there any thing interesting that you can say?

Lab Report

- In the lab write-up, be sure to include responses to the following questions as you discuss and analyze your results.
- What difference does the computational technique make on computed values?
- Does molecular bonding appear to play a role in computational accuracy?
- What differences are there between the computed values and literature values?
- How does one account for the difference among computed values?
- How does one account for the difference between computed and literature values?
- Propose at least two instances where computed data may be useful in an experimental laboratory setting.
- For H_2 , HCl and HF compare the electron distribution for these three molecules. What does this say about electronegativity?
- For H_2 , HCl and HF examine the vibrations for the three molecules and compare. Which molecule has the greatest vibrational frequency? Is there any relationship between the vibrational frequency to the electronegativity difference between the elements?
- For the four aromatic molecules compare the electron distributions. What does this say about electronegativity and the ability of the groups to extract or donate charge to the ring?
- For the four aromatic molecules examine the vibrations for the three molecules and compare. Is there any thing interesting that you can say?

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1.7: Equation of State

Equation of State Experiment -- Temperature and Pressure Measurements of an Ideal Gas During Heating Within a Closed Container

EXPERIMENT DESCRIPTION: The Ideal Gas Equation of State

Purpose

The ideal gas equation of state ($pV = mRT$) provides a simple relationship between pressure, temperature, mass, and volume for gases at relatively low pressures and high temperatures. This experiment illustrates the application of the ideal gas equation and other equations of state to relate the properties of several gases contained in a rigid vessel with changes in temperature.

Assignment

A stainless steel pressure vessel with a volume of 1 liter will be instrumented with a pressure transducer and thermocouple to measure the gage pressure and temperature, respectively, of the air inside the vessel. You will need to select your vessel and confirm its volume. **How do you determine the volume of the vessel?** Use the Pasco™ temperature and pressure transducers to connect to the vessel and secure so that it is air-tight. **Check with your instructor for how to determine if a fitting is air tight.** Please consult the laboratory instructor regarding the appropriate compression fittings. **What is a compression fitting? How does it differ from other types of pipe fittings?**

The pressure transducer produces a voltage signal that can be related to the gage pressure in the cylinder by a calibration curve that is supplied with the instrument. Note that atmospheric pressure in Washington, DC is approximately 13.6 psia. The calibration curve for the pressure transducer is given by the following equation:

$$p = 4.3087(V \cdot V) - (13.1176 V) + 10.7276$$

where V equals the voltage output (volts) from pressure transducer, and p equals the absolute pressure (kPa).

The thermocouple in the pressure vessel is connected in series with a second thermocouple that is located in an ice bath that provides a reference temperature. The thermocouple pair produces a voltage signal that is related to the temperature (T) of the air in the pressure vessel by the following expression:

$$T = T_{ref} + \frac{V}{S}$$

where T_{ref} equals the ice bath reference temperature (0°C), V equals the voltage (volts) measured across the thermocouple pair, and S equals the thermocouple constant, $42.4 \mu\text{V}/^{\circ}\text{C}$.

A signal processor displays and records the voltage signals from both the pressure transducer and the thermocouple during the course of an experimental trial. In addition, the signal processor records the data in a data file that can be downloaded to other programs for data analysis and plotting.

The steps you should follow to carry out the experiment are as follows:

1. Turn on the signal analyzer. Identify the location of the "start" and "pause" buttons.
2. Make sure the pressure readings and ranges are appropriate. The signal analyzer should display two different plots of pressure and time and temperature and time. You will need to combine these data to plot pressure versus temperature at the same times for your system over a range of different temperatures.
3. Check to verify that your hot plate is operating.
4. Temperature profiles (repeat as needed in order to generate reliable statistics)
 - Press "start" to begin reading data, and then heat the pressure vessel by placing it on the hot plate. Continue heating the vessel until the temperature plateaus (The pressure will reach approximately 400 kPa).
 - Create a slush using crushed dry ice or a liquid nitrogen slurry to cool the vessel to temperatures of at least -40°C . Record the data as above.

NOTE: Review the handling of cryogenics below before proceeding.

- Repeat for at least three gases

NOTE: DO NOT place a hot vessel into the cryogen or an extremely cold vessel into the heat bath.

5. Save the data appearing on the display onto a disk (ask the instructor for help if needed). Choose a meaningful name such as "yourname_LabTemp.dat" for the files. You may have to save two sets of data--one for temperature and another for pressure.
6. Using the data obtained in both the cooling and heating experiments, construct a P-T curve for the entire range of temperatures.

Handling of Cryogenics

Cryogenic Materials will be defined here as any material used for cooling baths that has a melting point, boiling point or sustained temperature below -20°C . This includes dry ice (solid CO_2), dry ice-isopropanol mixture, frozen slush baths prepared from liquid nitrogen and organic liquids (methanol, ethanol, hexane, toluene, etc.) and liquid nitrogen.

Handling Procedure:

When cryogenic liquids are transferred to containers located above waist-height of the operator the liquid must first be poured from the storage Dewar into a small, easily handled, insulated container (such as a glass Dewar flask) and then poured into the final container. The operator must wear a face shield in addition to safety glasses when pouring cryogenic liquids above waist-level. All containers with evacuated wall space (Dewar flasks) and evacuated round-bottom flasks that have volume of greater than 500 ml. must be wrapped with tape or surrounded by protective net to contain flying glass in case the container should break while being cooled with cryogenic liquid. Only round bottom flasks should be used for freezing and thawing of organic liquids. Evacuated flasks containing liquids frozen at cryogenic temperatures must be contained in another vessel (a beaker or open dish capable of holding the entire contents of the flask at all times).

Preparation of a Dry Ice Slurry:

The best low temperature baths are made with as high a percentage as possible of the coolant (dry ice here, or ice in general). Approximately the amount of dry ice that will be needed should be crushed and placed in the container (usually a dewar or equivalent). To this you should add the acetone or isopropanol slowly. This is most conveniently done with a squeeze bottle. Add only enough to cover the dry ice. If you need a looser slurry, this can be accomplished by addition of more solvent.

Loose slurries can be made in the following way:

A suitable container, usually a Dewar flask is filled about one-fourth to one-third full of the solvent. Acetone and isopropanol are both often used, but isopropanol is less volatile, less toxic, and is less flammable. A little crushed dry ice is added to the solvent and vigorous bubbling will result. As the dry ice sublimates and the solvent cools, the bubbling will become less violent. A little more dry ice can be added at this point. It should be remembered that the temperature of this bath will not be as low as with the previous recipe.

Dry ice can be added to either bath as needed to maintain the low temperature. When finished using the slurry, allow the dry ice to sublime completely, pour the solvent into a bottle indicating the solvent is for cold baths only. Loosely cap the container for about 24 hours or overnight to prevent a degassing mishap.

Analysis

- Using the initial values of the measured pressure and temperature, the volume of the vessel, calculate, from the ideal equation of state, the mass of air in the vessel. Assuming the volume and mass are constant during the heating process, calculate the temperature of the air (from the ideal gas equation) for each of the pressure values--remember that the recorded values of the pressure are absolute. Plot the experimental and calculated temperatures as a function of the measured pressure. Clearly label the graphs. Compare the experimental results with the theoretical results. What might be responsible for the differences?
- Plot the P vs T curves for each graph and compare the slopes to the value nR/V . Perform an error analysis based on the comparison of the theoretical and observed values. What differences do you see? Which gas or molecular characteristics might be responsible for the differences?
- Which of your gases might best be described by a [van der Waals equation of state](#)? Compare your P vs T curve to the van der Waals P vs T curve over the same range of T and P for each potential van der Waals gas. Discuss the similarities and differences.

What might be responsible for the differences?

- Extract an estimate of the van der Waals constant from your graphs. How do they compare to the literature values? How might you improve your results?

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1.8: Heat Capacity Ratios for Gases (C_p/C_v)

Measuring the Ratio of the Heat Capacity at Constant Pressure to the Heat Capacity at Constant Volume for a Gas (C_p/C_v)

Introduction

The equipartition theorem states that any quadratic energy term such as kinetic energy contributes equally to the internal energy of a system in thermal equilibrium. This means that for a gas each degree of freedom contributes $\frac{1}{2} RT$ to the internal energy on a molar basis (R is the ideal gas constant)

An atom of a monoatomic gas can move in three independent directions so the gas has three degrees of freedom due to its translational motion. Therefore its internal energy, U , follows the equation $U = \frac{3}{2} RT$. The heat capacity at constant volume, C_v , is the derivative of the internal energy with respect to the temperature, so for our monoatomic gas, $C_v = \frac{3}{2} R$.

The heat capacity at constant pressure can be estimated because the difference between the molar C_p and C_v is R ; $C_p - C_v = R$. Although this is strictly true for an ideal gas it is a good approximation for real gases.

The rotation of gas molecules adds additional degrees of freedom. A linear molecule rotates along two independent axes. Therefore a linear molecule has two rotational degrees of freedom. The total number of degrees of freedom for a linear molecule is 5 so its internal energy is $U = \frac{5}{2} RT$, its molar heat capacity at constant volume is $C_v = \frac{5}{2} R$ and its molar heat capacity at constant pressure will be $C_p = \frac{7}{2} R$.

A nonlinear molecule rotates along three independent axes. Therefore a linear molecule has three rotational degrees of freedom. The total number of degrees of freedom for a linear molecule is 6 so its internal energy is $U = 3 RT$, its molar heat capacity at constant volume is $C_v = 3 R$ and its molar heat capacity at constant pressure will be $C_p = 4 R$.

Vibrations may add to the heat capacity but only if they are thermally accessible. The vibrational temperature, Θ_{vib} , is defined by the equation:

$$\Theta_{vib} = \frac{hcv}{k}$$

where h is Planck's constant, c is the speed of light, v is the frequency and k is Boltzmann's constant. The vibrational contribution to the molar heat capacity from a given vibrational degree of freedom of frequency v is given by:

$$(C_v)_{vib} = N \times R \times \left(\frac{\Theta_{vib}}{T} \right)^2 \times \frac{\exp(\Theta_{vib}/T)}{\{\exp(\Theta_{vib}/T) - 1\}^2}$$

where N is the number of moles, R is the ideal gas constant and T is temperature. The total contribution to the heat capacity at constant volume from all vibrational degrees of freedom is:

$$C_{vib,Total} = \sum (C_v)_{vib}$$

where the summation is over all vibrational degrees of freedom, $3N-5$ (linear molecules) or $3N-6$ (non-linear molecules)

Experimental

You have a large bottle fitted with a gas inlet and a pressure gauge attached to a stopper in the neck of the bottle, Figure 1.

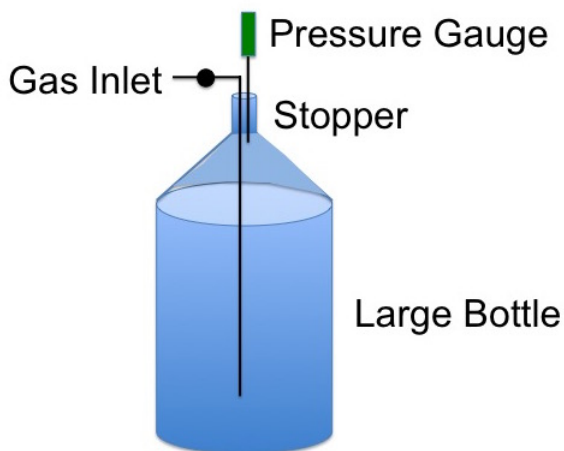


Figure 1. Setup for measuring the ratio of C_p/C_v for gases.

Now you begin with the gas at atmospheric pressure (760 Torr) and then add gas to increase the pressure inside the bottle by a small amount, say 1.5% (11.4 Torr).

Now very quickly pop the stopper from the bottleneck and return it very quickly to its original position, Figure 2.

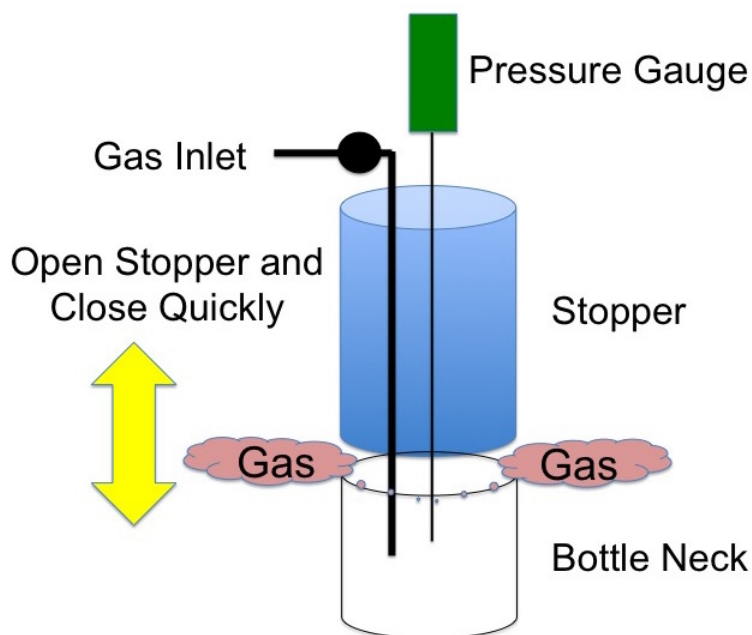


Figure 2. Remove the stopper very quickly.

Before reading further pause for a moment and consider the following two questions. What happens to the pressure and temperature in the bottle when you remove the stopper? How will the pressure and temperature change over the next few minutes? Note that the bottle is not thermally isolated from its surroundings.

First the gas returns to the ambient atmospheric pressure when you remove the stopper from the bottle and gas escapes. Assuming you remove the stopper and return it quickly, this process is adiabatic. An adiabatic process is a process where heat is not transferred ($dq = 0$). When the gas expands it does work against its surroundings and it cools a little.

Second after a few minutes the gas returns to the original ambient temperature because the bottle is not thermally isolated. What

does this do to its pressure? The pressure rises because of the ideal gas law, $PV=nRT$. Rearranging we have $P=nRT/V$. As the temperature of the gas returns to ambient the pressure rises.

The extent of the pressure increase is related to the ratio of the gas's heat capacity at constant pressure to its heat capacity at constant volume. This ratio is given by:

$$\frac{C_p}{C_v} = \frac{\ln P_1 - \ln P_2}{\ln P_1 - \ln P_3}$$

Where P_1 is the initial pressure of the gas, P_2 is the ambient pressure of the room and P_3 is the final pressure reached after the stopper is popped.

Procedure

Construct an apparatus as described above. Gases will be assigned in class and may include nitrogen, oxygen, helium, argon and carbon dioxide. Perform the experiment 10 times for each assign gas. Calculate the mean and standard deviations for your measurements. Compare your measurements of C_p/C_v with available literature values and values calculated from the Equipartition of Energy Theorem.

1.8: Heat Capacity Ratios for Gases (C_p/C_v) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

1.9: Chemical Garden - Introduction to Research

Physical Chemistry Laboratory

Introduction to Research – Measuring the Growth Rate of Tendrils in a “Chemical Garden”

Introduction

Download the following paper: J.H.E. Cartwright, B. Escibano, and C.I. Sainz-Díaz, 2011, Chemical-Garden Formation, Morphology, and Composition. I. Effect of the Nature of the Cations, *Langmuir*, 27, 3286–3293 as an introduction. When you put crystals of some metal salts you get the formation and growth of “tendrils”, Figure 1.



Figure 1. A metallic silicate tendril growing from a crystal in a sodium silicate solution.

The goal of this laboratory is to give you the opportunity to think like researcher scientists. Today's problem is to how to measure the growth rate of the tendrils under a couple of conditions. Each group may attack this problem in any reasonable way. Creativity is encouraged.

Procedure

You will be given a copper salt and an unknown crystal. You may place these in two test tubes or beaker and add a solution of sodium silicate (please conserve the sodium silicate because we have only a limited amount). You will want to record the time you add the solution. Tendrils should form almost immediately.

You can define the growth rate of the tendrils in at least two ways: 1) the millimeters the length increases per second and 2) the increase in mass of a tendrils per second. In both cases you will need the start time when you added the solution. You may try to use a ruler to measure the growth rate as in the first definition. You may weigh a tendril after it has grown and divide by the total time to get the mass increase per second as for definition 2. Are there other definitions of growth rate? Can pictures or movies taken with your smart phones/tablets/computers useful? Be creative and think before you do the experiments. You have two laboratory periods to work on these experiments.

Laboratory Report

You will report your results in the standard laboratory report format. In the introduction discuss what you find on the chemistry of the formation of the chemical gardens. You have one paper already but please search for more. Present your procedure in the Experimental section. This is what you decide to do in the laboratory – don't copy this write-up! Present your results and discussion/conclusions as usual.

GOOD LUCK with this Research Project!

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1.10: Blackbody Radiation

CHEM 174 Physical Chemistry Laboratory II

Blackbody Radiation

Classical mechanics failed as scientists examined nature on smaller and smaller spatial scales. There were five experimental observations that were of particular importance for the development of quantum mechanics.

First Experiments that Established Quantum Mechanics

1. Blackbody Radiation
2. Photoelectric Effect
3. Atomic and Molecular Spectroscopy
4. Heat Capacities at Low Temperature
5. Electron Diffraction

Blackbody radiation was one of the first experiments that led to quantum mechanics. It started with the simple observation that when you heat a metal that it first becomes red, followed by yellow and then white hot as the temperature increases. Now, imagine a cube with a tiny pinhole that leads to a very irregular cavity inside the cube. As the Figure 1 shows, any light reaching the pinhole is very likely to be absorbed before it can exit the pinhole.

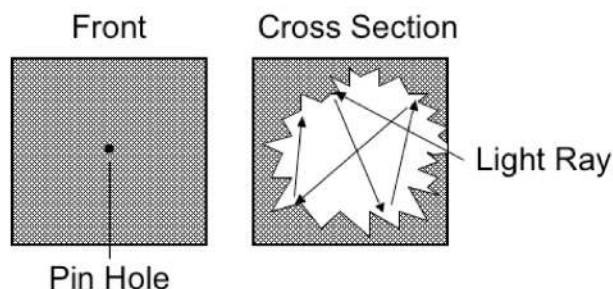


Figure 1. An idealized blackbody radiator

Any object in thermal equilibrium is constantly emitting and absorbing radiation. Kirchhoff's Law states that a body that radiates strongly at some wavelength also absorbs radiation strongly at the same wavelength. Therefore an ideal blackbody radiator is both a perfect absorber and emitter of radiation. Many thermal sources, such as the sun, a flame, an incandescent light bulb, the Earth, approximate blackbody radiators. However, if you use only classical physics, the radiation from a blackbody radiator is impossible to describe correctly without quantum mechanics.

Careful measurements that used experimental approximations to the ideal blackbody radiator showed that the radiation distribution depends only on the temperature of the body. The hotter the temperature the greater the radiation and the lower the wavelength of the peak, Figure 2.

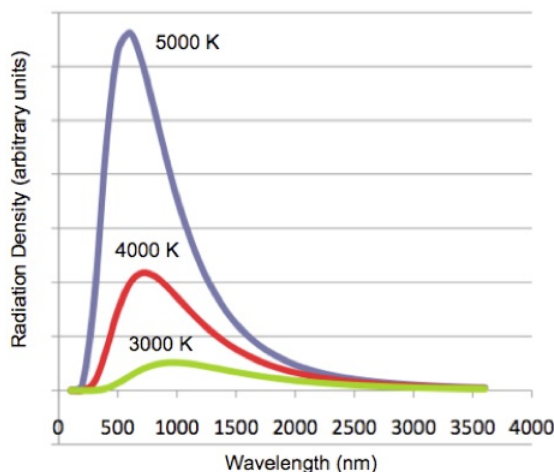


Figure 2. Blackbody radiation for three different temperatures.

The radiation distribution $B(T)$ is:

Equation (1)

$$B_{\lambda}(T) = \frac{3.74 \times 10^{-16} \lambda^{-5}}{\pi (\exp(1.45 \times 10^{-2} / (\lambda T)) - 1)}$$

The radiation peak, $\lambda_{\max}$, is equal to:

Equation (2)

$$\lambda_{\max}(nm) = \frac{2.897 \times 10^6 (nmK)}{T(K)}$$

For a blackbody the power emitted per unit area, M , is:

Equation (3)

$$M = \sigma T^4$$

$$\sigma = 5.67 \times 10^{-8} W m^{-2} K^{-4}$$

A first attempt to explain these observations was made by Lord Rayleigh. He assumed that the thermal motions of atoms that compose the walls of the blackbody excite “oscillators” of the electromagnetic field. (For a very rough mental picture of his oscillators, think of the electromagnetic field as a vast series of strings on a musical instrument.) Next he applied the equipartition principle from statistical thermodynamics. The assumption was that all of the oscillators share equally in the energy supplied by the walls. According to the equipartition principle each oscillator gets kinetic energy of $\frac{1}{2} kT$ and potential energy of $\frac{1}{2} kT$ for a total of kT where: k is Boltzmann’s Constant (the gas constant divided by Avogadro’s number and the temperature, T). Even the oscillators with the highest frequencies such as x-rays and even more are excited. This reasoning led to the Rayleigh-Jeans Law where σ is the radiation density:

Equation (4)

$$dE = \delta d\lambda$$

$$\delta = \frac{8\pi kT}{\lambda^4}$$

The accumulation of energy in the highest frequencies leads to a severe problem with the Rayleigh-Jeans Law. As the wavelength gets shorter that amount of radiation becomes greater and greater, Figure 3. Everything in this world glows in the dark according to the Rayleigh-Jeans Law. If it were not for quantum effects a lighted match should emit x-rays intensely and even more gamma-rays! This incorrect prediction is called the “ultraviolet catastrophe.”

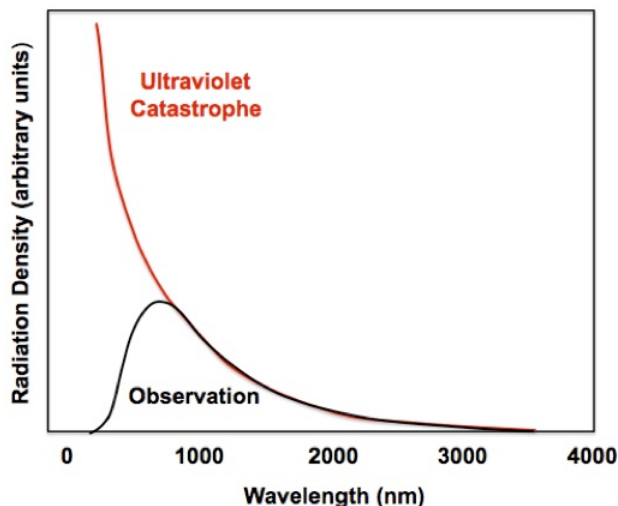


Figure 3. The ultraviolet catastrophe predicted by the Rayleigh-Jeans Law

The ultraviolet catastrophe makes no sense! Max Planck solved the problem by assuming that the energy appears in discrete (quantized) packages. He assumed that the energy, E , of an oscillator was equal to an integer multiplied by a constant, h (Planck's constant), times the frequency of the oscillator.

Equation (5)

$$E = nh\nu$$

$$n = 0, 1, 2, 3, \dots$$

If Equation 5 is correct then oscillators are excited only if they can get energy of at least $h\nu$. But as the frequency ν becomes greater it becomes more difficult for an oscillator to receive enough energy from the blackbody's walls. The maximum oscillator frequency excited depends only on the temperature of the walls. The net effect of assuming that energy is quantized eliminates the contribution of high-frequency oscillators to the emitted radiation and this eliminates the ultraviolet catastrophe. The blackbody radiation predicted from the quantum theory of Max Planck conforms to Equations 1 – 3.

In this laboratory you will investigate the effect of temperature on the location of the peak of the blackbody radiation curve.

Procedure

Required Equipment

Ocean Optics UV-Vis Spectrometer

Blackbody Radiator Experimental Setup

Candle

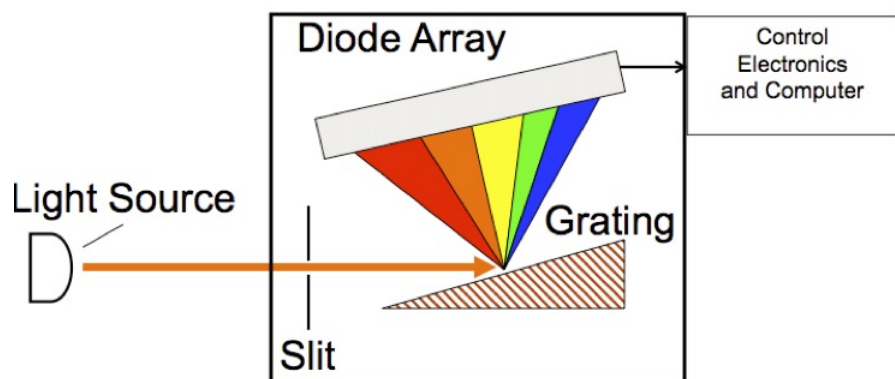


Figure 4. Schematic diagram of Ocean Optics UV-Vis spectrometer

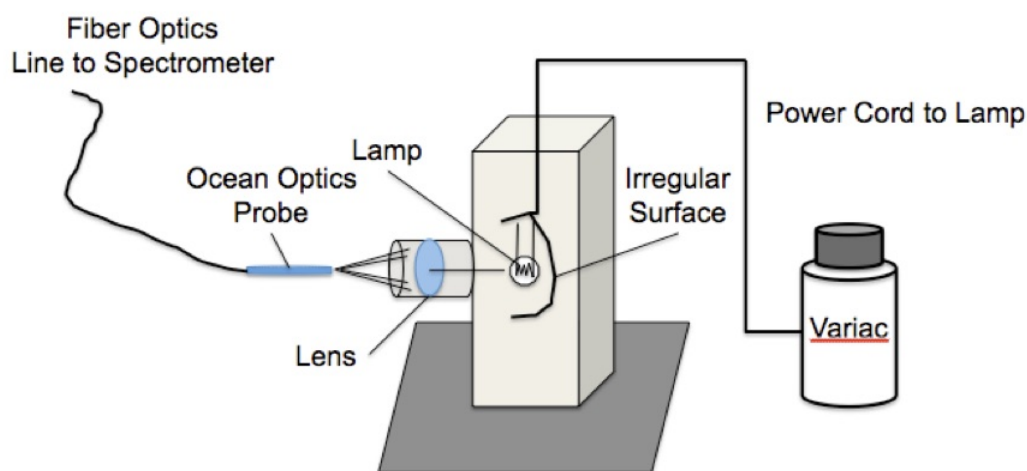


Figure 5. Blackbody radiator experimental setup

Blackbody Radiation Measurements

The procedure is to make at observations of the emission spectrum of the light emitted from the blackbody radiation setup with the Ocean Optics UV-Vis Spectrometer. Vary the setting of the power Variac and take spectra.

Candle Radiation Measurements

The procedure is to make at observations of the emission spectrum of the light emitted from a candle flame with the Ocean Optics UV-Vis Spectrometer. Take spectra of different sections of the flame (lower blue, middle, upper most...). **Be careful, do not put the lens of the optical probe in the candle flame.**

Calculations

- Use the calibration equations given in class to correct the measured wavelength scale using the calibration equation that you got from the calibration laboratory to get the true wavelengths for the blackbody and candle spectra.
- Plot each of the blackbody radiation spectra. The x-axis will be the true wavelength in nm and the y-axis will be emission intensity.
- Determine the peak of the radiation distribution, λ_{max} , for all your spectra.
- Plot the peak of the radiation distribution, λ_{max} , as a function of the variac setting.
- Use Equation (2) to calculate the temperature of the blackbody for each variac setting. Plot the temperature (y-axis) as a function of the variac setting (x-axis).

- Taking the temperatures calculated in step 5, use Equation (3) to calculate the power per unit area emitted by the blackbody for each variac setting. Plot the power per unit area (y-axis) as a function of the variac setting (x-axis).
- Discuss your blackbody results in view of Equation (1).
- Use the blackbody equations to estimate the temperature of the various sections of the flame.
- [Report](#)

Please follow the standard format for a scientific paper given in the syllabus and discussed in lecture. It includes the following.

- Abstract – A summary of the entire experiment
- Short Introduction describing the purpose and any relevant theory you find.
- Experimental with a short description of the apparatus and procedures.
- Results please tabulate your observations.
- Discussion and Conclusions Can you find other relevant observations? Compare your results with other available observations. Please discuss the answers to the questions (below) here.
- References. Cite all sources including books, peer reviewed journals and the internet. I am happiest when you find more than two.
- Appendix with a photocopy of the raw data as you entered them in your notebook. I do not need copies of all the spectrometer data, an example first page of one spectrum would be good (total 1 page).

Reference

- Atkins, P. and J. De Paula, Physical Chemistry, Eighth Edition W. H. Freeman, 2006.

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1.11: Atomic Spectroscopy

CHEM 174 Physical Chemistry Laboratory II

Atomic Spectra

The Hydrogen-Like Atom

A hydrogen-like atom is composed of a single electron and a nucleus with an arbitrary number of protons. In this laboratory the relationship between the wavelengths of light emitted from atoms and changes in quantum numbers will be explored.

Schrödinger's equation in three dimensions is:

Equation (1)

$$\hat{H}\psi = E\psi$$
$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r, \theta, \varphi)$$

Where: $\hat{H}$ is the Hamiltonian, ψ is the wavefunction, E represents the possible energy levels, $\hbar$ is Planck's constant, h , divided by 2π , m is the particle's mass. r, θ, φ are the spatial coordinates and $V(r, \theta, \varphi)$ is the potential energy.

A nucleus with an atomic number Z has a charge of Ze where: e is the unit of elementary charge (the charge on a single proton or electron). Coulomb's Law gives the force between an electron and the nucleus of an atom. Therefore the potential energy of an electron separated from the nucleus by a distance r is given by Equation (2) where ϵ_0 is the vacuum permittivity:

Equation (2)

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

Equation (3) is Schrödinger equation for the internal motion of an electron relative to its nucleus.

Equation (3)

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi$$
$$\mu = \frac{1}{m_e} + \frac{1}{m_N}$$

Where m_e is the mass of the electron and m_N is the mass of the nucleus.

The solution of Equation (3) yields the energy levels given by Equation (4).

Equation (4)

$$E_n = \frac{Z^2\mu e^4}{32\pi^2\epsilon_0^2\hbar^2 n^2}$$

if:

$$R_H = \frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}$$

Then:

$$E_n = \frac{Z^2 R_H}{n^2}$$

R_H in Equation (4) is known as the Rydberg constant, $R_H = 109,677 \text{ cm}^{-1}$. Energy levels for the hydrogen-like atom are plotted in Figure 1.

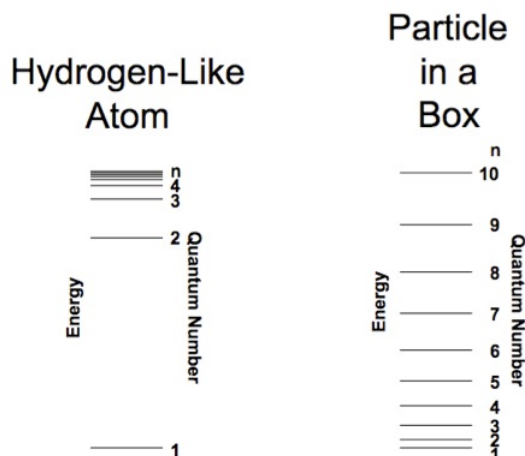


Figure 1. The energy levels of a hydrogen-like atom are shown compared with the energy levels of the particle in a box.

If an electron in an atom is excited to a higher energy level by passing an electric current a photon will be emitted when it falls to a lower energy level. The energy difference between the initial energy level and the final energy level is given by Equation (5). In Equation (5) n_f is the final energy level (lower energy) and n_i is the initial energy level (higher energy).

Equation (5)

$$E_n = Z^2 R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

or

$$\frac{1}{\lambda_n} = Z^2 R'_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

A series of lines arises when electrons fall from higher energy levels to the same lower energy level, Figure 2. For the hydrogen atom when the final quantum number (n_f) is 1 you have the Lyman series, when $n_f = 2$ you have the Balmer series and when $n_f = 3$ you have the Paschen series. The series that you can see in the visible is the Balmer series.

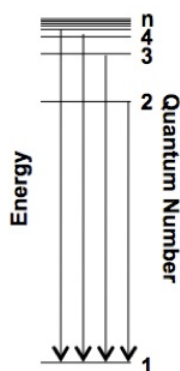


Figure 2. The Lyman Series is the series where $n_f = 1$, the excited electron falls into the ground state.

Procedure

1. Calculate the Rydberg constant in cm^{-1} from the hydrogen lines in the Balmer series. These lines are the ones that you used in previous laboratories: 410.17, 434.05, 486.13 and 656.28 nm.

- First, convert the units of the emitted lines from wavelengths to cm^{-1} :

Equation (6)

$$\frac{1}{\lambda(\text{cm})} = \frac{1}{\lambda(\text{nm}) \times 10^7 \text{cm}}$$

- Note that the final quantum number for the Balmer series is 2. Therefore the initial quantum numbers must be greater than 2. The initial quantum numbers are 3, 4, 5 and 6. Match the initial quantum number with the correct emission above. To do this correctly think about which transition is the most energetic and with transition is the least.
 - Now use Excel or similar application to plot $\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$; as the x-axis and $\frac{1}{\lambda(\text{cm})}$; as the y-axis. You will get a very straight line.
 - Determine the slope and intercept. The slope is the Rydberg constant. Note that it should be near $R_H = 109,677 \text{ cm}^{-1}$.
2. Recalibrate your spectrometer using the calibration standard provided. The optical probe may be attached to the calibration standard by a screw fitting. The standard provides a mixture of Ar and Hg lines. The known wavelengths are given on the back of the calibration standard. Take a few spectra at different intensities. Make a new calibration curve using as many of the lines that you can identify from the calibration standard.
3. Take emission spectra of the Hg lamp at different intensities.
- Correct the measured emission line wavelengths of Hg using your new calibration curve.
 - Convert the units of the emitted lines from wavelengths to cm^{-1} by using Equation (6).
 - Identify as many of the spectral lines as you can by using the NIST database at:
<http://physics.nist.gov/PhysRefData/ASD/index.html>
4. Take emission spectra of the Ne lamp at different intensities. Repeat all of the steps in part 3 for Ne.
5. Take emission spectra of the Ar lamp at different intensities. Repeat all of the steps in part 3 for Ar.

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1.12: UV-Vis Absorption Spectroscopy

CHEM 174 Physical Chemistry Laboratory II

Visible Absorption Spectroscopy and Beer's Law

Theory: Beers Law

Beer's law describes how radiation interacts with matter. A completely transparent container contains some compound and there is an incident monochromatic radiation beam of intensity I_0 . The greater the concentration of the compound and the longer the path length, L , the lower the intensity of the emerging beam, I .

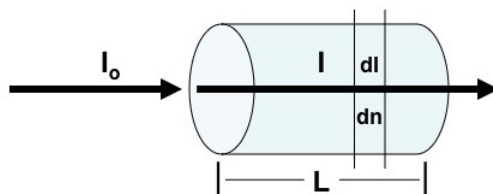


Figure 1. A cell containing a substance that absorbs radiation and the definition of terms needed to derive Beer's Law.

A more precise way of saying this is that "successive increments in the number of identical absorbing molecules in the path of a beam of monochromatic radiation absorb equal fractions of the radiant energy transversing them" (Ewing, 1969). Mathematically dI is the change of radiation intensity at intensity I caused by the absorbance of dn molecules with σ as a proportionally constant.

$$\frac{dI}{dn} = -\sigma I$$

This equation can be rearranged and integrated between the limits of I_0 to I and 0 to N where N is the total number of molecules transversed.

$$\int_{I_0}^I \frac{dI}{I} = -\sigma \int_0^N dn$$

$$\ln(I) - \ln(I_0) = -\sigma N$$

$$\ln\left(\frac{I_0}{I}\right) = \sigma N$$

The absorbance, A , is defined as:

$$A = \ln\left(\frac{I_0}{I}\right)$$

The number N is more conveniently written as the product of the concentration $[C]$ and the path length, L . Beer's Law is then:

$$A = [C]\sigma L$$

If $[C]$ is expressed in molecules cm^{-3} and L in cm then σ is the absorption cross section per molecule cm^2 . Note: Divide a concentration in moles liter $^{-1}$ by 1×10^3 to convert to moles cm^{-3} .

Electronic Absorption and Dipole Strength

Molecules only absorb photons that lead to a change of state. Visible radiation typically corresponds to changes in electronic states. For example the figure below shows two different electronic states, ψ_m and ψ_n , rotational states represented by the horizontal lined and two possible transitions between the electronic states.

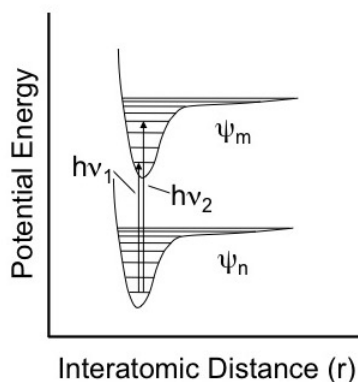


Figure 2. Absorption of visible or ultraviolet radiation between two stable electronic states.

In general the stronger absorbances are related to stronger dipole moments and a greater degree of overlap between the lower and upper states. The strength of the transition is proportional to the following integral where $\hat{\mu}$ is the dipole moment operator.

$$f \propto \int \psi_n \hat{\mu} \psi_m dz$$

In this lab we will quantitatively determine the absorption cross sections for Congo Red. This compound is an acid base indicator that is blue-violet in acidic solutions and red at higher pH. "Its spectral properties can be approximated by the quantum mechanical particle in a box" (see the lab lecture). Congo Red is composed of four aromatic rings and two $-N=N-$ groups. Its structure is given below.

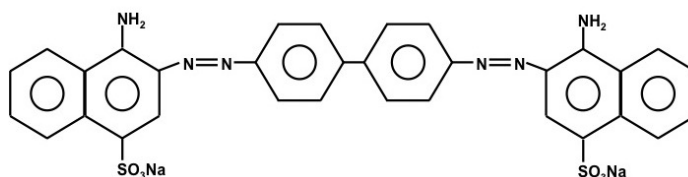


Figure 3. The chemical structure of Congo Red. The molecular weight of Congo Red is $696.67 \text{ g mole}^{-1}$.

Procedure

1. An aqueous stock solution (Red) of Congo Red solution has been prepared at pH 7 with a concentration of about 7.5×10^{-5} moles liter $^{-1}$.
2. Prepare series of dilute solutions by quantitatively diluting the Red stock solution to make 5 or 6 solutions. Use a 1 or 2 ml pipet to transfer different increments of the solution to small volumetric flasks and fill with distilled water.

Note: In the following work completely clean the cuvette between samples. Use the same spectrometer settings and the same cuvette for the background and the Congo Red solutions.

3. Fill a cuvette with distilled water and record a spectrum. This spectrum will be your first background spectrum (I_0).
4. Record a spectrum of the stock Congo Red solution.
5. Wash the cuvette and fill it with distilled water and record a spectrum. This spectrum will be your second background spectrum (I_0).
6. Repeat steps 3 to 5 for each of the more dilute solutions.
7. Finally after running all the solutions fill the cuvette with distilled water and record one more background spectrum.
8. An acidified (Blue-Violet) aqueous stock solution of Congo Red solution has been prepared with a concentration of about 1.5×10^{-7} moles liter $^{-1}$. A small amount of acetic acid with used to acidify the solution. Prepare series of dilute solutions by quantitatively diluting the Blue-Violet stock solution to make 5 or 6 solutions. Use a 1 or 2 ml pipet to transfer different increments of the solution to small volumetric flasks and fill with distilled water.

Repeat all the steps to take spectra for the blue violet Congo Red solution.

Calculations

Calculate absorbance spectra for the dye solutions by taking the natural log of the ratio between the background spectra and the Congo Red solutions.

$$A = \ln \left(\frac{I_o}{I} \right)$$

For the background spectrum (I_o) average the background taken before and after the Congo Red spectrum.

Correct the wavelength scale using the calibrations you developed during the calibration laboratory.

Plot the spectra. Make one set of plots for the Red Congo Red solution and another set of plots for the Blue-Violet Congo Red solution.

For both sets of solutions determine the numerical value of the extinction coefficient for the maximum absorption peak, λ_{max} , by plotting the absorbance as a function of the concentration for both sets of solutions. Determine the slope of the best-fit line and the correlation coefficient for both plots. The slope is the product of the maximum extinction coefficient and the path length (1 cm). Divide the slope by 1 cm to get the maximum extinction coefficient and its unit will be liter mole⁻¹ cm⁻¹.

Convert the extinction coefficient (liter mole⁻¹ cm⁻¹) to the cross section of one molecule σ_{max} . Multiply by the conversion factors 10³ cm³/ 1 liter and 1 mole / 6.02 × 10²³ molecules. The units should now be in cm² molecule⁻¹.

Take the ratio of σ_{max} to the measured absorbance at λ_{max} . Multiply the absorbances for each spectra by this ratio to determine the cross sections for all the wavelengths.

Average the spectra after you calculated the cross sections to get a single spectrum of cross sections. Calculate the average and the standard deviation of the cross sections as a function of the wavelengths for the Red and for the Blue-Violet Congo Red solutions.

Questions for Discussion Section in Your Report

1. Why is it necessary to calibrate the wavelength scale but not the light intensity measurement for this experiment?
2. Which form of Congo Red has the greatest σ_{max} ?

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1.13: Particle in a Box

CHEM 174 Physical Chemistry Laboratory II

Dye Color, the Particle in a Box and

Determination of the Length of a Molecular System

Purpose

The objectives of this experiment include:

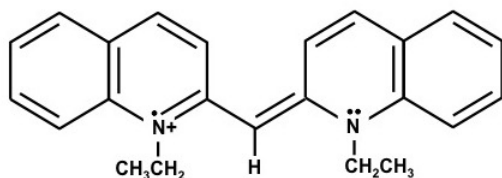
- Learning more about how organic compounds absorb radiation.
- Why compounds have color.
- How spectroscopic measurements may be used to derive some molecular properties (in this case the length of a conjugated pi-bonded system in dye molecules).

Introduction

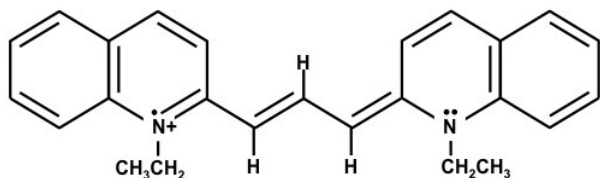
White light is a mixture of all wavelengths of the visible spectrum. Color results when a compound absorbs light in a portion of the visible spectrum and transmits (or reflects) the remainder. Absorption of blue light produces the color red while the absorption of red light produces the color blue-green. Therefore to understand how organic dyes produce color it is necessary to understand how these compounds absorb light.

Consider the following series of cyanine dyes (I- is not shown in each case below):

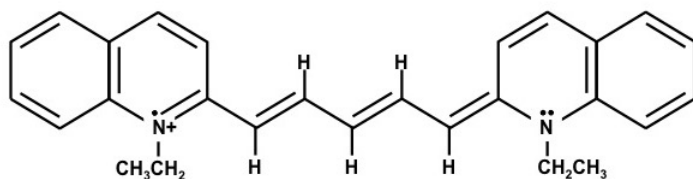
1,1'-Diethyl-2,2'-cyanine iodide – (Dye A)



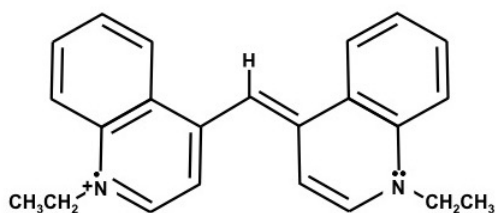
1,1'-Diethyl-2,2'-carbocyanine iodide – (Dye B)



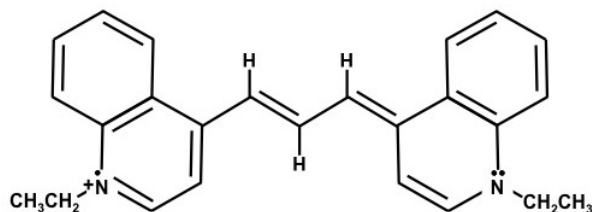
1,1'-Diethyl-2,2'-dicarbocyanine iodide – (Dye C)



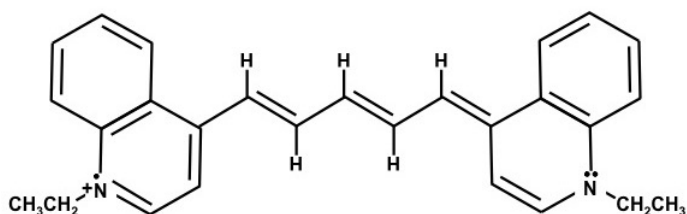
1,1'-Diethyl-4,4'-cyanine iodide – (Dye D)



1,1'-Diethyl-4,4'-carbocyanine iodide – (Dye E)



1,1'-Diethyl-4,4'-dicarbocyanine iodide – (Dye F)



The chemical structures are resonance structures; the positive charge can be equally well represented as residing on either nitrogen atom. In reality the pi electrons may be considered to reside across the system of conjugated pi-bond system that extends from one nitrogen atom to the other, Figure 1. The conjugated pi-bonded system extends above and below the plane of the sigma bonds.

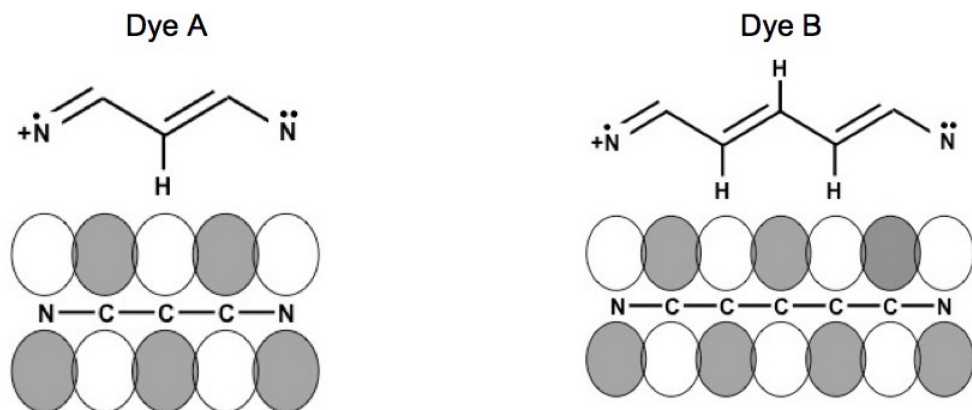


Figure 1. Conjugated pi-bonded system for dyes A and B.

Electrons change energy levels when radiation is absorbed. Schrödinger's equation is used to calculate the energy levels, Equation (1).

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x) \psi = E \psi$$

where: $\hbar$ is Planck's constant divided by 2π , m is the particle's mass, $V(x)$ is the system's potential energy, ψ is the wave function and E represents the possible energy levels.

The potential energy of a system needs to be defined to calculate the energy levels. Figure 2 shows the potential energy of the

conjugated pi-bonded systems for dyes A and B. Figure 2 shows that there is a potential energy barrier at the nitrogen atoms and there are “wells” at each atom; however to a reasonable degree of accuracy the potential energy of the conjugated pi-bonded system can be approximated by a particle in a box potential.

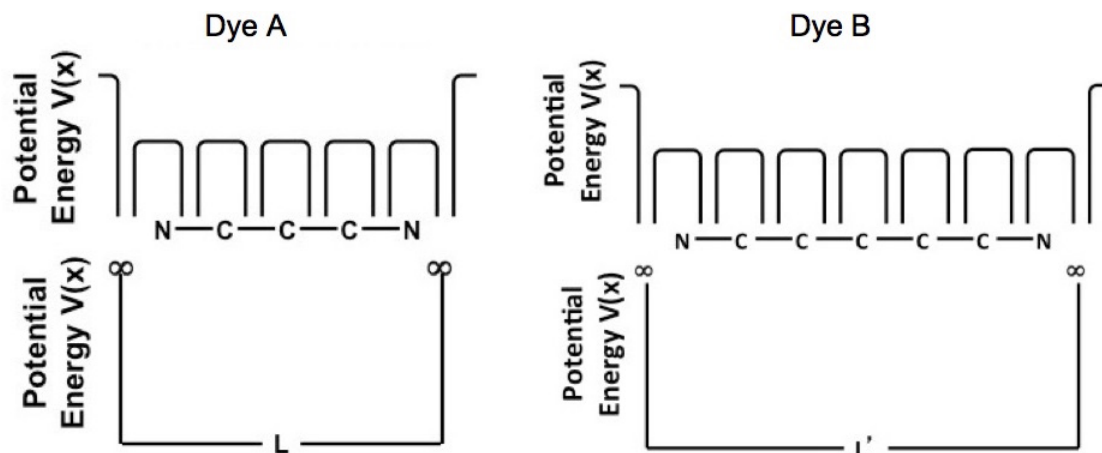


Figure 2. Potential energy of the conjugated pi-bond system for dyes A and B.

The solution of Schrödinger's equation for the particle in a box yields the energy levels given by Equation (2).

$$E = n^2 \frac{h^2}{8mL^2}$$

$$n = 1, 2, 3, \dots$$

where: E represents the possible energy levels h is Planck's constant, m is the particle's mass and L is the length of the box.

Pauli Exclusion Principle and Packing Electrons into the Particle in a Box

Dye A has 6 electrons and dye B has 8 electrons in their respective pi-bond systems. If the particle in a box is used to represent these molecules then the pi electrons need to be distributed into the box. The Pauli exclusion principle and the energy levels establish the electron distribution.

An electron is a fermion and the Pauli Principle states that the total wave function for a system of fermions must be antisymmetric when particles are interchanged. Suppose the total wave function is $\psi(q_1, q_2, q_3, \dots)$ where $q_1, q_2, q_3, \dots$ are the coordinates / quantum numbers of electrons 1, 2, 3, ... If electrons 1 and 2 are exchanged:

$$\psi(q_1, q_2, q_3, q_4, \dots) = -\psi(q_2, q_1, q_3, q_4, \dots)$$

Suppose there were two electrons with the same set of quantum numbers (q_1), then the total wave function would be $\psi(q_1, q_1, q_3, \dots)$. If the two electrons with the same set of quantum numbers were switched then Equation (4) results.

$$\psi(q_1, q_1, q_3, q_4, \dots) = -\psi(q_1, q_1, q_3, q_4, \dots)$$

For any function, $f(x)$, if $f(x) = -f(x)$ then $f(x)$ must be equal to zero. If $\psi(q_1, q_1, q_3, \dots)$ is equal to zero then probability of any two electrons having the same identical set of quantum numbers is zero.

In the case of electrons in the particle in a box there are two quantum numbers, n and spin. The quantum number $n = 1, 2, 3, \dots$ and

the spin of an electron can be either up (+1/2) or down (-1/2). So each level of the particle in a box can contain two electrons, one spin up and the other spin down. Figure 3 shows how pi electrons for dye A (a 6 electron system) and dye B (a 8 electron system) are contained in the box when it is in the ground state. Note that the energy levels are more closely spaced due to the fact that dye B is represented by a larger box.

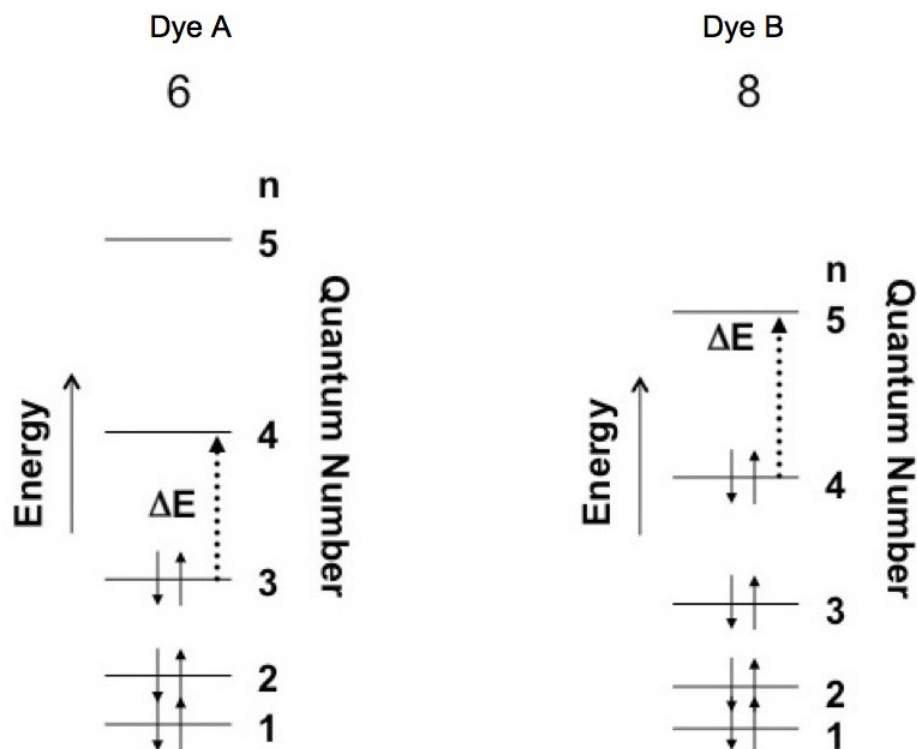


Figure 3. Assignment of electrons into particle in a box model for dyes A and B. The figure also shows the change in state caused by the absorption of a photon.

Dye A Dye B

Absorption of Energy

The change in energy associated with an electron jumping from one state to another is given by equation (5).

$$\Delta E = \frac{h^2}{8mL^2} (n_f^2 - n_i^2)$$

where: ΔE is the change in energy, h is Planck's constant, m is the mass of the electron, L is the length of the box and n_i and n_f are the initial and final quantum numbers.

Three things need to be considered to calculate the energy changes from Equation 5. For the dyes studied in this experiment the number of electrons (N) is an even number, p. There will be two electrons per energy level because of the Pauli Exclusion Principle. The principle quantum number changes by +1. Mathematically:

Equations (6 - 9)

$$p = n_i = \frac{N}{2}$$

$$n_f = n_i + 1$$

$$\Delta E = \frac{h^2}{8mL^2} [(p+1)^2 - p^2]$$

$$\Delta E = \frac{h^2}{8mL^2} (2p + 1)$$

Remembering that:

$$\lambda_{abs} = \frac{hc}{\Delta E}$$

where λ_{abs} is the wavelength of the absorbed radiation and c is the speed of light, the following equations result.

$$\lambda_{abs} = \frac{8mL^2c}{h(2p + 1)}$$

or Equation (11)

$$L = \sqrt{\frac{\lambda_{abs}h(2p + 1)}{8mc}}$$

In the experiment the length of the conjugated pi-system will be calculated for each dye from measurements of λ_{abs} and Equation (11).

Safety

All six dyes: 1,1'-Diethyl-4,4'-cyanine iodide, 1,1'-Diethyl-4,4'-carbocyanine iodide, 1,1'-Diethyl-4,4'-dicarbocyanine iodide, 1,1'-Diethyl-2,2'-cyanine iodide, 1,1'-Diethyl-2,2'-carbocyanine iodide and 1,1'-Diethyl-2,2'-dicarbocyanine iodide and methanol are considered highly toxic and irritate the skin. Do not get the dye solutions or methanol on your skin or in your eyes. Wear eye protection.

Procedure

1. Solutions of dyes A – F in methanol have been prepared.

Note: In the following work completely clean the cuvette between samples. Use the same spectrometer settings and the same cuvette for the background and the dye solutions. Also do not cross contaminate the dye solutions by the using same pipette to transfer different dye solutions.

2. Fill a cuvette with methanol and record a spectrum. This spectrum will be your background spectrum (I_o) for this dye.
3. Add a drop or two dye A solution. You should just be able to see a little color.
4. Wash the cuvette. Go back to step 3
5. Repeat steps 3 – 5 until spectra have been recorded for all the dye solutions.

Calculations

- Calculate absorbance spectra for the dye solutions by taking the natural log of the ratio between the background spectra and the dye solutions.

$$A = \ln \left(\frac{I_o}{I} \right)$$

- Correct the wavelength scale using the calibrations given in the class handout.
- Make plots of the absorbance spectra for dyes A – F. You may combine the plots in one or two page graphs.

Fill out the worksheet given below as you do the following.

- Identify the color of each dye.
- Identify the wavelength of the maximum absorbance, λ_{max} , for each dye.
- Count the number of pi-electrons, N .
- Calculate the length of the conjugated pi-system, L , for each of the dyes from the measured λ_{max} and Equation (11). Provide a sample calculation in your report.

- Count the number of bonds in the conjugated pi-system for each dye.
- Assume that each bond has a length of 0.139 nm and estimate the length of the box from the number of bonds. Provide a sample calculation in your report
- Evaluate and tabulate the difference between the length of the box calculated from Equation (11) and the length estimated from the number of bonds for each dye.

Report and Questions

1. For the recalibration include a plot of the known wavelengths as a function of the measured wavelengths and the linear fit with your report.
2. Discuss the observed colors and the absorption spectra. What is the relationship between the dye colors and the spectra?
3. Make two plots of $\lambda_{\max}$ as a function of the length of the box calculated from Equation (11): one plot for dyes A – C and another for D – F.
4. Discuss the difference between the length of the box calculated from Equation (11) and the length estimated from the number of bonds. Is the difference usually positive or negative? Suggest reasons for this difference.

Reference

McRae, E.G. and M. Kasha (1958). J. Chem. Phys. 28, 721.

Pope, M., C.E. Swenberg, Electronic Processes in Organic Crystals, (Oxford University Press, New York, 1982), Chapter 1D.

New Mexico State University, Department of Chemistry

<http://www.chemistry.nmsu.edu/studntres/chem435/Lab5/>

Worksheet for particle in a box; include with your report.

Name _____

Dye	Color	$\lambda_{\max}(\text{nm})$	Number of pi-electrons N	Experimental box length (nm)	Number of bonds in conjugated system	Predicted box length (nm)	Difference Experimental – Predicted (nm)
A							
B							
C							
D							
E							
F							

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1.14: Fourier Transform Infrared Spectroscopy (FTIR)

CHEM 174 Physical Chemistry Laboratory II

Fourier Transform Infrared Spectroscopy (FTIR)

How a Fourier Transform Infrared Spectrometer Works

There are many advantages to a Fourier Transform Infrared Spectrometer (FTIR): higher resolution at lower cost, relatively less time to collect spectra, for reacting systems the spectra are easier to interpret and FTIR can be used in a mode (photoacoustic) where samples do not have to be optically thin.

A Fourier Transform Infrared Spectrometer (FTIR) is based on the interferometer. The interferometer in an FTIR works on the same principles as the one used in the Michelson–Morley experiment. The Michelson–Morley showed that the speed of light is the same in all directions; a key finding supporting special relativity. Figure 1 shows a schematic of an interferometer.

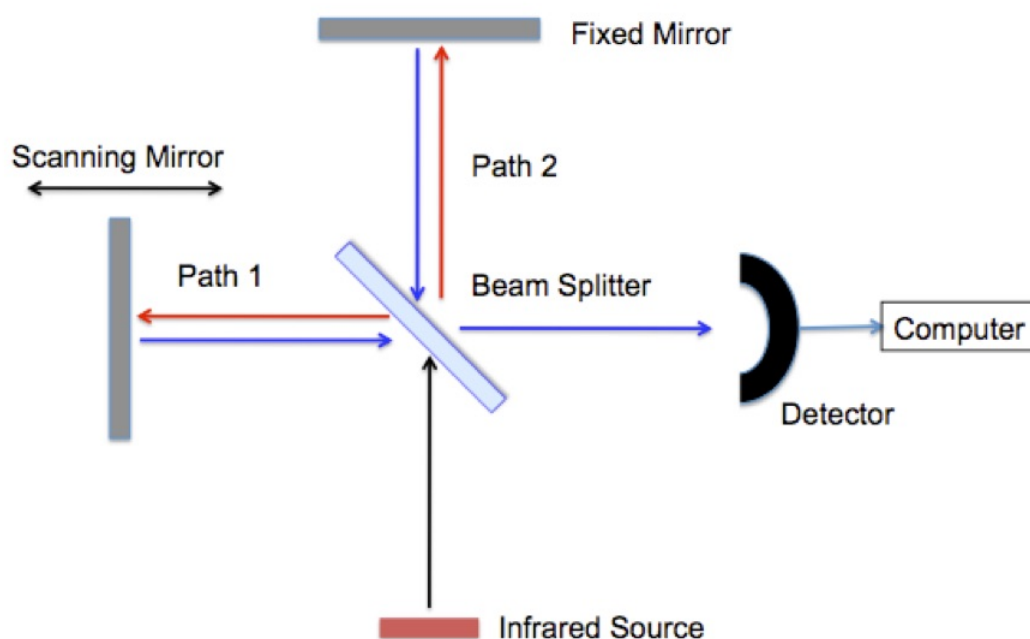


Figure 1. A schematic of an interferometer used in a Fourier Transfer Infrared Spectrometer (FTIR).

Infrared radiation is typically generated by passing electricity through a conducting ceramic bar (glow bar). First the radiation reaches a “beam splitter”. The beam splitter is a partially coated mirror that reflects half of the infrared radiation and passes the remaining half. The radiation follows either path 1 or path 2 to mirrors that return it to the beam splitter where the beams recombine and they are reflected in to an infrared detector. Remember that the radiation is a wave, Figure 2. The signal seen at the detector at any moment in time depends on the difference between path 1 and path 2.

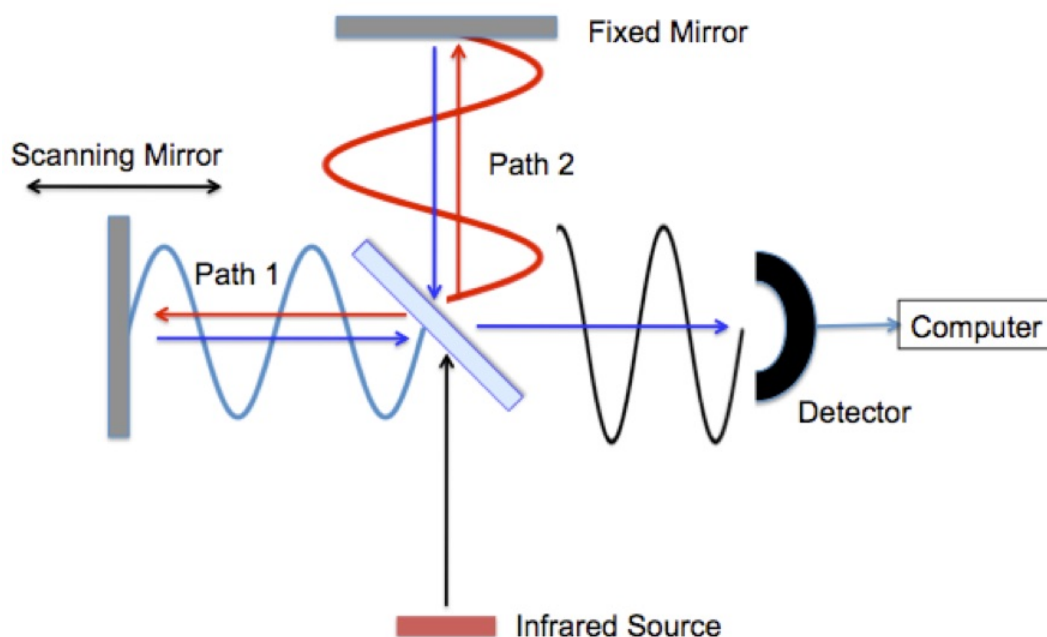


Figure 2. FTIR interferometer with radiation waves drawn in.

Suppose for a moment that we use a laser that emits a single wavelength as the radiation source. Next suppose that the lengths of path 1 and path 2 are both even multiples of the laser's radiation wavelength. When the radiation returns to the beam splitter it arrives "in phase", the beams reinforce each other when they recombine and a strong signal will be seen at the detector, Figure 1A. This process is called "constructive interference".

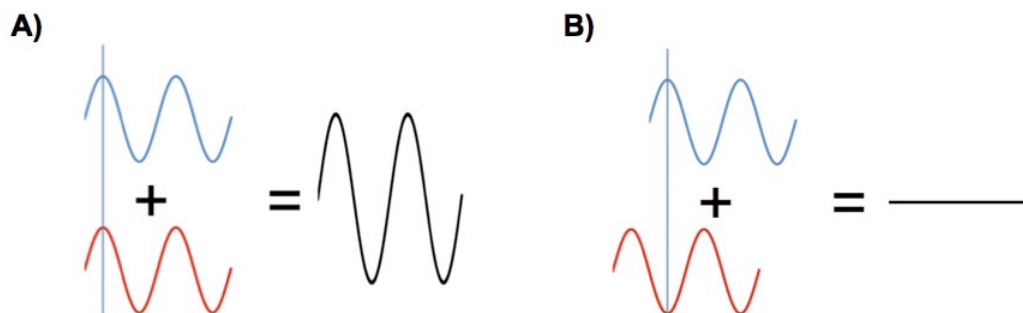


Figure 3. (A) Constructive interference by two recombining radiation beams. (B) Destructive interference by two recombining radiation beams.

Suppose that the scanning mirror on path 1 is moved a distance equal to half of the wavelength of the laser radiation. Now when the beams recombine at the beam splitter they will "out of phase" and destructively interfere cancelling each other and no signal will be seen at the detector. If the scanning mirror is scanned at a constant rate a sinusoidal signal is generated at the detector.

The frequency of the detector signal depends on the speed of the mirror and wavelength of the radiation. Let infrared radiation with a frequency of 1000 cm^{-1} pass through the interferometer and move the scanning mirror with a speed of 1 cm s^{-1} . There will be 1000 waves of infrared radiation per centimeter for this frequency (this is why cm^{-1} is called sometimes "wave-numbers"). If the mirror is moved a total of 1 cm then there will be 1000 cycles of constructive and destructive interference. For these conditions the frequency of the detector signal will be $1000\text{ cm}^{-1} \times 1\text{ cm s}^{-1} = 1000\text{ s}^{-1}$. The important point is that the scanning information has coded the wavelength of the infrared radiation so that the detector can measure frequency and intensity at the same time. An

infrared detector is very capable of detecting the intensity and the frequency of an infrared signal with an audio frequency.

When multiple frequencies pass through the interferometer, the signal at the detector is the sum of the coded frequencies. A glow bar is a ceramic that emits infrared radiation when heated by an electric current. It is an excellent approximation to a blackbody radiator, Figure 4A. When this radiation passes through the interferometer the signals add, “the superposition”, of all the signals is observed at the detector, Figure 4B. Figure 4B is called an “interferogram”. Note that the information contained in a spectrum and the interferogram is identical.

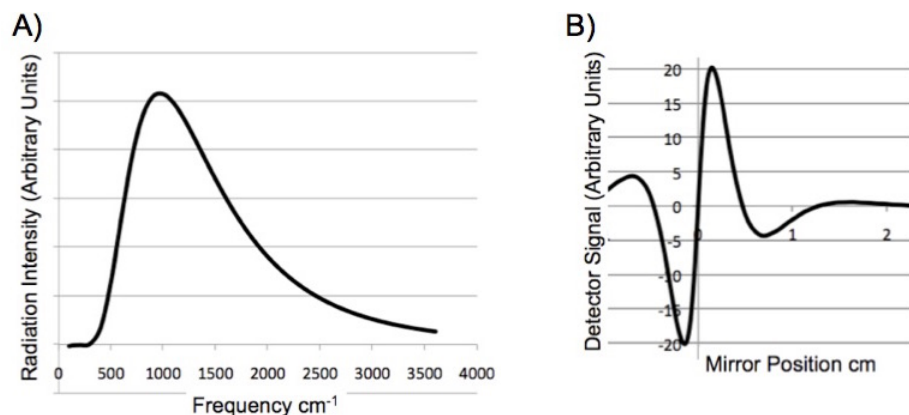


Figure 4. (A) Blackbody radiation spectrum of a glow bar. (B) The signal seen at the detector of an FTIR as a function of the scanning mirror position.

Although the information contained in a spectrum and the interferogram is identical chemists find it difficult to interpret interferogram in terms of molecular structure. The interferogram measured by the FTIR must be converted back to a spectrum. This transformation is accomplished by applying the Fourier transform to the interferogram. Equation (1) shows the Fourier transform.

$$\tilde{f}(\nu) = \int_{-\infty}^{\infty} f(x) e^{-2i\pi\nu x} dx$$

where: $f(x)$ is the signal measured at the detector which is a function of the mirror position, x , $\tilde{f}(\nu)$ is the spectrum which is a function of frequency, ν . Figure 5 shows a sample function and its Fourier transform.

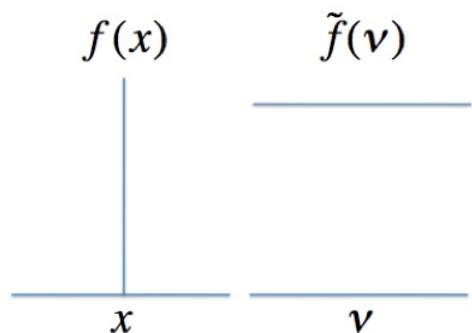


Figure 5. The Fourier transform of a delta function, $f(x)$, is a horizontal line, $\tilde{f}(\nu)$. The more highly $f(x)$ is defined in space the less defined is $\tilde{f}(\nu)$. The Heisenberg Uncertainty Principle is a consequence of this relationship.

To calculate a spectrum from an interferogram considerable computational resources are required and therefore Fourier transformation methods came into widespread use only after the invention of modern computers.

Procedure

This report will be combined with the next laboratory session. Please take the spectra as a group and discuss together. But please – each person will submit their own individual report.

For all of the spectra gathered save ASCII copies to disk and take with you.

1. Record a spectrum of a standard polyethylene sample.
2. Record a gas-phase spectrum of air using an evacuated cell as the reference.
3. Record a gas-phase spectrum of acetaldehyde using an air filled cell as the reference. Expose to UV light for an hour and run a second spectrum.
4. Record a liquid-phase spectrum of acetaldehyde using attenuated total reflection (ATR) with air as the reference.
5. Record a spectrum of solid Congo Red using ATR with air as the reference.

Analysis

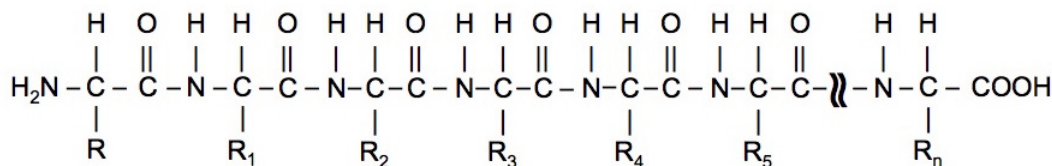
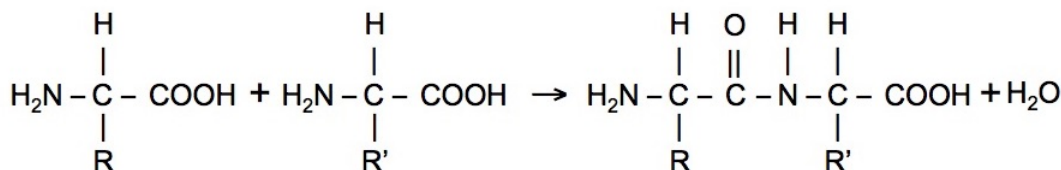
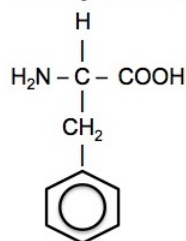
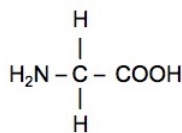
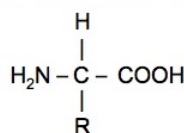
This report will be combined with the next laboratory. For all of the spectra gathered save ASCII copies to disk and take with you.

1. Use the measured IR lines of the standard polyethylene sample to check the wavelength calibration.
2. Identify as many of the IR bands/lines for as many atmospheric gases as you can in the air spectrum. Do you expect to see Ar, O₂ and N₂?
3. Discuss the bands found in the IR spectra of acetaldehyde. What differences do you see between the gas and liquid-phase spectra?
4. For the gas-phase acetaldehyde sample what are the differences in the spectra before and after the sample was exposed to UV radiation? If there are differences, what happened?
5. Discuss the IR spectrum of Congo Red. Is there any relationship between the pi-chain and the observed IR spectrum? What are the differences in the functional groups between the particle-in-a-box-experiment dyes (Laboratory 13) and the Congo Red dye? Are these groups in Congo Red seen in its IR spectra?

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Biomaterials: Protein Structure Determination by FTIR Spectroscopy

The goal of this research is to investigate the effects of environmental stressors on proteins. Proteins are among the most important structural components of living cells and they are biological polymers composed of amino acids. An amino acid has both an amine group (-NH_2) and a carboxyl group (-COOH). A generic representation of an amino acid and the simplest of the series, glycine, are shown below.



Molecules vibrate, rotate and stretch at characteristic frequencies when they absorb infrared radiation. These frequencies are determined by structure of the molecule. We have used infrared spectroscopy to examine protein structure and the effects toxic compounds on proteins.

Procedure

Fourier transform infrared spectroscopy will be used in a total internal reflectance mode in this study. An advantage of total internal reflectance is that a solution containing a sample only needed to be placed on top of an infrared window. Problems with the large infrared absorption by water are avoided and no cells to contain the solutions are required.

Record an FT-IR spectrum of the simplest amino acid, glycine, to see the infrared absorption due to the amino and carboxyl acid groups. Record spectra of both glycine crystals and an aqueous-phase solution.

Next record infrared spectra of solid-phase gelatin and of a gelatin solution. Gelatin is composed of the protein collagen. Mix the gelatin solution with methanol; a white precipitate should result showing that the protein was denatured. Record infrared spectra of the precipitate and also record an FT-IR of methanol for comparison.

Summary of procedure:

Part A: Take FT-IR spectra of:

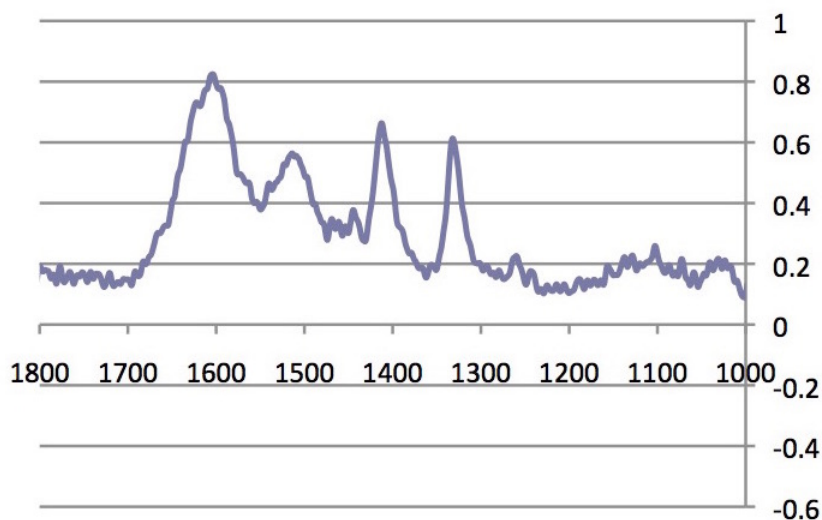
1. Glycine in solid phase.
2. Collagen protein in solid phase.
3. Glycine in aqueous phase.
4. Collagen in aqueous phase.
5. Denature the collagen by adding a small amount of methanol. Take FT-IR spectra of the precipitate. Take an FT-IR of methanol

Some Sample IR Spectra

Note that the absorbance of the highest peak in the complete spectrum was normalized to 1.00; below only the range between 1000 and 1800 cm^{-1} are shown.

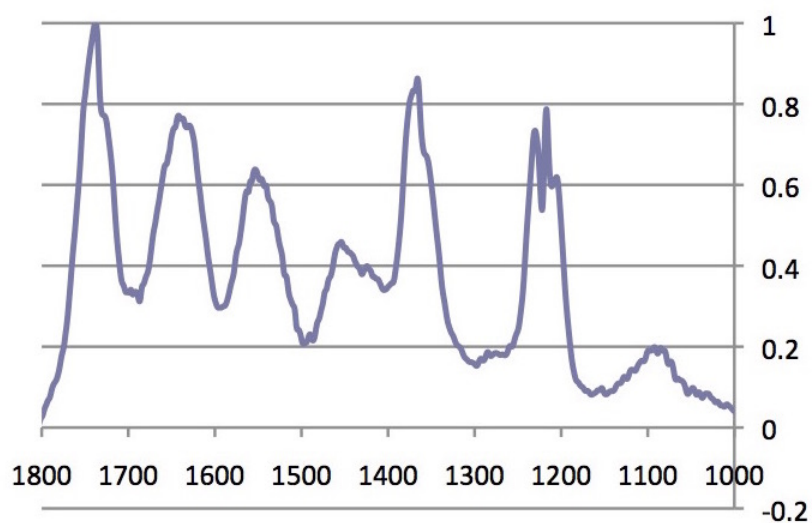
Aqueous-phase

Glycine



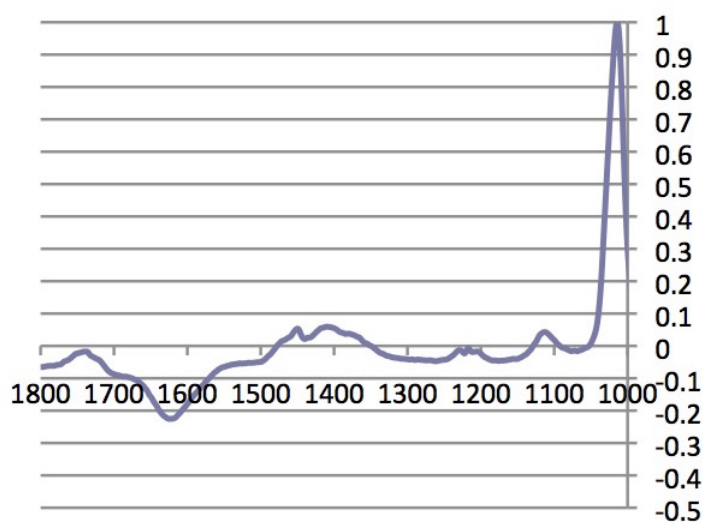
Aqueous-phase

Gelatine



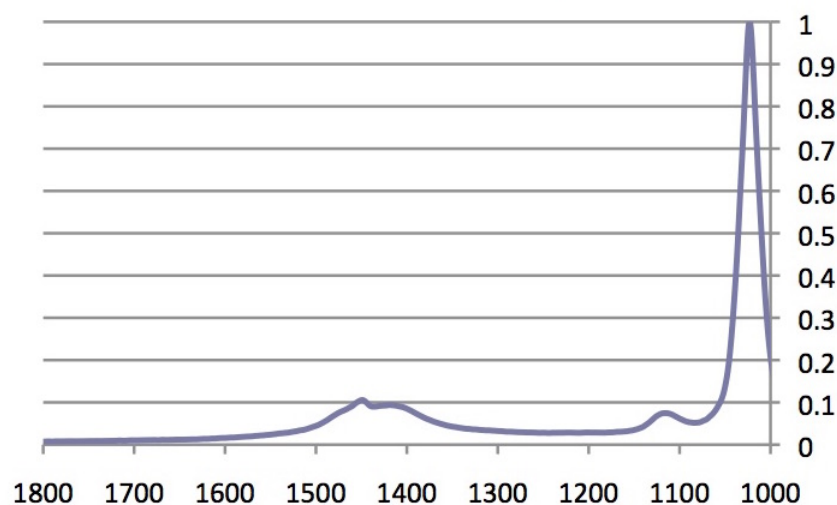
Precipitate

Gelatine + MeOH



Liquid-phase

MeOH



Report

- Use the research journal article format and discuss your results by answering the following questions in your report:
- What are the similarities and differences between the spectra of glycine, collagen and the denatured participate?
- Are there any differences between the solid and aqueous phase spectra?
- What can you say about the relationship between the protein's functional groups and the absorbance peaks in the spectra? You may need to do some literature research to answer this question.

References

Nielson, D.L. and M.M. Cox, "Lehninger Principles of Biochemistry" 4ed., Freeman, 2005.

Alberts, B., A. Johnson, J. Lewis, M. Raff, K. Roberts and P. Walter, "Molecular Biology of The Cell" 5ed., Garland Science, 2008.

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1.16: Biomaterials- Studies of Protein Structure by Computational Quantum Chemistry

CHEM 174 Physical Chemistry Laboratory II

Biomaterials: Studies of Protein Structure by Computational Quantum Chemistry

Introduction

You already become familiar Spartan. In this lab you will use it to:

- 1) Calculate an IR spectra of Glycine, Alanine, Leucine and Valine
- 2) Calculate an IR spectra of polyglycine
- 3) Examine the difference between an α -helix and a β -sheet.

Procedure

Part 1 Glycine Example

Go into Spartan and select a new simulation. Click on the Peptide tab on the model entry toolbox. Click "Gly" to bring up glycine at the top of the toolbox. Click on the main screen to bring up glycine on the main model window.

Now you need to terminate the glycine so click terminate. For simplicity on the calculate be sure that the terminate option is set to yield a neutral molecule.

You are ready to set up the calculation. Enter calculations and choose the Hartree-Fock 3-21G model, choose single energy and click the IR box, also keep the molecule neutral. Submit the calculation under a name that you choose.

When the calculation is complete view the IR spectra and note the IR bands that were calculated. Repeat for the other amino acids

Compare the glycine calculation with your spectra for solid glycine from the previous laboratory and discuss in your laboratory report.

Part 2. Triglycine

Repeat for triglycine. Note that it would be better if the calculation was performed for a larger peptide but triglycine is already a little time consuming. You will compare this calculation with your spectra for solid collagen.

Part 3. α -Helix and β -Sheets

1. Use Spartan to construct a peptide with at least 20 amino acids (your choice). Transfer it to the screen as an α -helix. Save an image of the structure for your report and discuss its appearance.
2. Use Spartan to construct the same peptide and transfer it to the screen as a β -sheet. Save an image of the structure for your report and discuss its appearance.

Report

Use the research journal article format.

Discuss your results by answering the following questions in the discussion section of your report.

- For glycine, compare the individually computed vibrational frequencies to those observed (from the previous laboratory) in your experimental spectrum.
- Which vibrational motions produced the most intense peaks in your observed glycine spectrum? Is this consistent with the theoretical prediction?
- Compare the theoretical frequencies of glycine to those of the other amino acids. What are the similarities and what are the differences?
- For all the calculated spectra what can you say about the relationship between the functional groups and the absorbance peaks?
- How many peaks can you identify as being common between the different amino acids?
- You probably noticed that the same group (e.g. C=O stretching) in different molecules might have shifted significantly. By significantly, we mean by more than 2x the spectral resolution. Which group frequency shifted the most between your

molecules? In what direction, relative to the Glycine frequencies, is the shift? (Lower energy or higher energy) Offer an explanation for this behavior.

- Perform some statistical analysis on the vibrational frequencies of the different amino acids based on literature data (average absolute error, standard deviation, and variance).
- What are the similarities and differences between the calculated spectra of glycine and triglycine?
- What are the similarities and differences between the calculated spectra of glycine and your measured glycine IR?
- What are the similarities and differences between the calculated spectra of triglycine and your measured collagen IR? Clearly the spectra will not be the same but can you say anything about the trend?
- Discuss the major differences between peptides with α -helix and β -sheet structures.
- Overall, discuss your impressions on the utility of IR spectroscopy as a probe of protein structure: “thumbs up”, “thumbs down”, or something in between?

Reference

Spartan '04 Windows: Tutorial and User's Guide, Wavefunction, Irvine, CA, 2004, pages 102 – 105.

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1.17: Nano-Particles and Quantum Dots

CHEM 174 Physical Chemistry Laboratory II

Nano-Particles, Quantum Dots and Emission Spectroscopy

Introduction

Nano-technology is the science and engineering of devices with a size range between 1 to 100 nm. Substances in this size range may have properties that are different than those in the bulk. For example the semiconductor cadmium phosphide in the bulk is black but smaller particles can be red, orange, yellow or white depending upon their size (Brown et al., 2009). The smallest particles are white.

Quantum dots are very small aggregates of semiconductor material that contain 10^3 to 10^5 atoms and are between 1 to 10 nm in diameter. For quantum dots prepared from a given substance, their color and electrical properties can be tuned by varying their size. They have potential applications in biology and medicine, photovoltaic electricity generation, light sources and display devices and computing. Their applications to biological problems are among the most significant. Organic dyes have a long history of applications to problems in microscopy, analysis and the treatment of disease. Quantum dots can be engineered to specifications much more precisely than traditional organic dyes. They provide a very intense light when excited and they are very stable, they may persist for months in a biological system. Applications include, tagging of cells and their real-time observation of cells over long time periods, in-vitro imaging of cells (Dahan et al. 2003; Ballou et al., 2004) and the delivery of gene-silencing molecules into cells (Newsome, 2008). The latter is an example of a potential therapeutic application of quantum dots. The major potential drawbacks are toxicity and other environmental effects that are not yet well known.

Semiconductors

Covalent bonds are formed from the overlap of atomic orbitals. When the bonds are formed both bonding and anti-bonding molecular orbitals are formed. For every bonding molecular orbital there is an anti-bonding molecular orbital formed. When a p-orbital overlaps with another p-orbital three bonding molecular orbital and three anti-bonding molecular orbitals are formed. In a crystal the bonding molecular orbitals constitute the valence band and anti-bonding orbitals constitute the conduction band. The difference in energy between the valence band and the conduction band is called the band gap, Figure 1.

In metals the band gap is very low and there is a population of electrons in the conduction band. These are the electrons that conduct electricity. The band gap is greater in semiconductors and few electrons are found in the conduction band. The absorption of a photon may promote an electron from the valence band to the conduction band. This excitation of the electron from the valence band creates "hole" in the valence band. Conversely the recombination of an electron and a hole may result in light emission; this is the basis of the light-emitting diode, Figure 2.

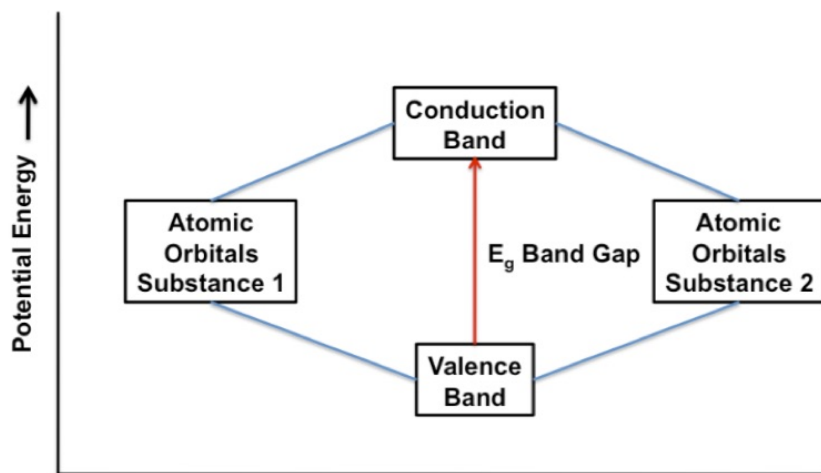


Figure 1. The figure shows the formation of bonding (valence band) and anti-bonding molecular orbitals (conduction band) from atomic orbitals. The band gap is the potential energy difference between the valence and conduction band.

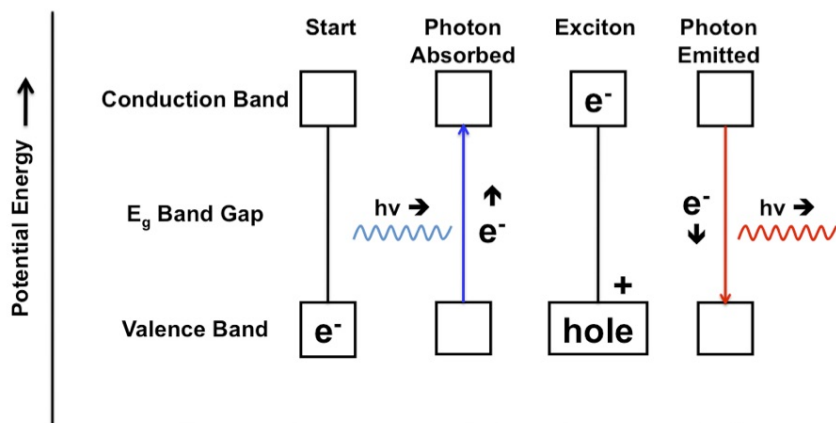


Figure 2. An electron is initially in the ground state. Next a photon with energy at least equal to the band gap is absorbed and the electron is promoted from the valence band to the conduction band. A hole is left behind. (Note that while there is a net positive charge left behind, it is not correct to call the hole positive.) The electron and hole pair together is called an exciton. Finally the electron will return to valence band and a photon is emitted.

Quantum Mechanics

In the laboratory “Dye Color, the Particle in a Box and Determination of the Length of a Molecular System,” the quantum mechanics of a particle in a linear box was presented. Schrödinger’s equation in one dimension is Equation (1)

$$\hat{H}\psi = E\psi$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

where: $\hat{H}$ is the Hamiltonian, ψ is the wavefunction, E represents the possible energy levels, $\hbar$ is Planck’s constant, $\hbar$, divided by 2π , m is the particle’s mass, x is the spatial dimension and $V(x)$ is the potential energy.

For the particle in a box of length, L , the boundary conditions are $V(0) = +\infty$, $V(L) = +\infty$ and $V(x) = 0$ for $0 < x < L$. Solution of Equation (1) for these boundary conditions yields the energy levels given by Equation (2).

$$E = n^2 \frac{\hbar^2}{8mL^2}$$

$$n = 1, 2, 3, \dots$$

where: n are integers (quantum numbers).

The particle in a box can be extended to a three-dimensional sphere. The Hamiltonian for a spherical particle in a box is given by Equation (3).

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2$$

In spherical coordinates the boundary condition is $V(r) = 0$ for $0 \leq r < R$ and $V(r) = +\infty$ for $r \geq R$ where: R is the radius of a sphere. The energy levels of a spherical particle in a box are given by Equation (4).

$$E = n^2 \frac{\hbar^2}{8mR^2}$$

$$n = 1, 2, 3 \dots$$

The approximate Hamiltonian for an exciton is similar to that for the spherical particle in a box but both the electron and the hole are confined within the quantum dot. In addition there is an electrostatic interaction between the electron and the hole that follows Coulomb's Law (Atkins and de Paula, 2006).

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{4\pi\epsilon |r_e - r_h|}$$

where: m_e is the mass of the electron, m_h is the mass of the hole, e is the charge of an electron, ϵ is the permittivity of the semiconductor and $|r_e - r_h|$ is the absolute value of the distance between the electron and the hole. The boundary conditions for exciton are the same as for the spherical particle in a box. The solution for the energy of an exciton, E_{ex} , is given by the following equation, (Atkins and de Paula, 2006).

$$E_{ex} = \frac{\hbar^2}{8R^2} \left(\frac{1}{m_e} - \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon R}$$

The band gap energy, E_g , is:

$$E_g = -\frac{1.8e^2}{4\pi\epsilon R}$$

$$E_g = \frac{E'}{R}$$

where

$$E' = -\frac{1.8e^2}{4\pi\epsilon}$$

$$E_{ex} = \frac{\hbar^2}{8R^2} \left(\frac{1}{m_e} - \frac{1}{m_h} \right) + \frac{E'}{R}$$

Exciton Creation and Emission

In this experiment quantum dots will be excited by blue light photons, emitted from a diode source, to form excitons. The excitons decay and when the electron recombines with the hole a photon with energy equal to E_{ex} is emitted. If the wavelength of the emitted photon is measured the radius of the quantum dot can be calculated starting with Equation (9) and Equation (10).

$$E = \frac{hc}{\lambda}$$

Equating Equations (9) and (10) yields the following Equation (11).

$$\frac{hc}{\lambda} = \frac{\hbar^2}{8R^2} \left(\frac{1}{m_e} - \frac{1}{m_h} \right) - \frac{E'}{R}$$

To determine the radius of the quantum dot from the wavelength of the exciton emission, multiply each term in Equation (11) by R^2 and rearrange to a quadratic form that may be solved by using the quadratic equation.

$$\frac{hcR^2}{\lambda} - E'R - \frac{\hbar^2}{8} \left(\frac{1}{m_e} - \frac{1}{m_h} \right) = 0$$

Let:

$$a = \frac{hcR^2}{\lambda}$$

$$b = -E'R$$

$$c = -\frac{\hbar^2}{8} \left(\frac{1}{m_e} - \frac{1}{m_h} \right)$$

Then:

$$R = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

or

$$R = \lambda \times \left(\frac{E' + \sqrt{E'^2 + \frac{\hbar^3 c}{2\lambda} \left(\frac{1}{m_e} - \frac{1}{m_h} \right)}}{2\hbar c} \right)$$

You may want to check the derivation of the final expression from the quadratic equation.

In your calculations use the following values:

Quantity	Value
$\hbar$	$6.626 \times 10^{-34} \text{ J s}$
c	$2.998 \times 10^8 \text{ m s}^{-1}$
m_e	$9.109 \times 10^{-31} \text{ kg}$
m_h	$6.830 \times 10^{-30} \text{ kg}$
E'	$8.750 \times 10^{-28} \text{ J m}$

Procedure

Required Equipment

Quantum dots (Four different sizes are provided in vials of solution).

Ocean Optics UV-Vis Spectrometer

Red and Blue Light Emitting Diodes

Backlight for Absorption Measurements

You will measure both absorption spectra and emission spectra of the quantum dots. You will use the emission spectra to calculate the radii of the four different sizes of quantum dots.

Absorption Spectra

1. Use the Ocean Optics spectrometer to take a background spectrum of the background light source, Figure 3.
2. Place the vials containing the quantum dots in front of the background light source.
3. Use the Ocean Optics spectrometer to record a spectrum of each vial.
4. For your report plot the spectra for each vial as absorption spectra $A = \ln \left(\frac{I_0}{I} \right)$. Use the background spectrum as your I_0 .

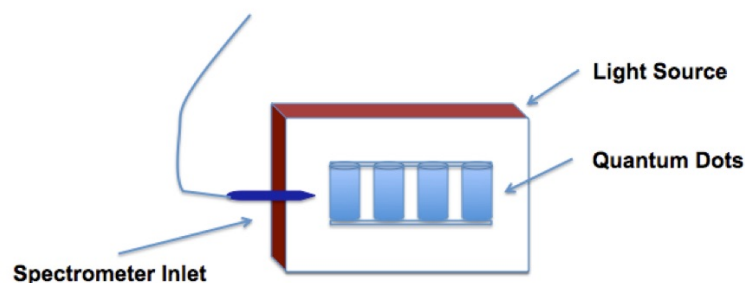


Figure 3. This figure shows the placement of light source, quantum dots and spectrometer inlet for absorption spectra.

Emission Spectra

1. Use a blue light emitting diode to excite the quantum dots. Use the Ocean Optics spectrometer to take a spectrum of the blue light emitting diode. Do not point the diode directly into the spectrometer optical fiber. Rather reflect the light in to the spectrometer by using a white surface such as a piece of paper.
2. Place the blue light emitting diode below a vial and turn it on, Figure 4.
3. Use the Ocean Optics spectrometer to record an emission spectrum of the vial.
4. Repeat steps 3 and 4 until you have done all four vials.

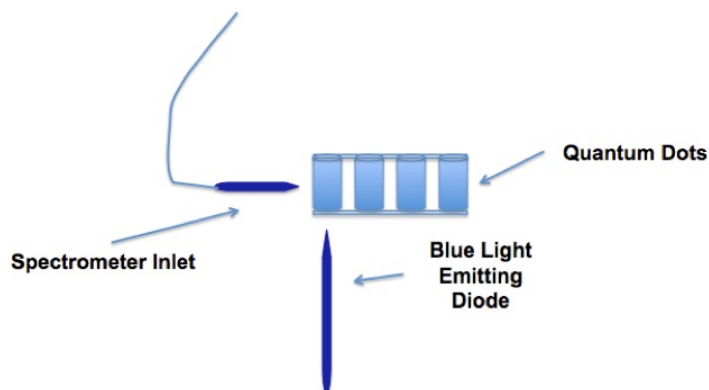


Figure 4. This figure shows the placement of blue light emitting diode, quantum dots and spectrometer inlet for emission spectra of the excitons.

Calculations, Questions and Report

Use your wavelength calibration curve to determine the calibrated wavelength scale for all of your measured spectra. This includes the absorption spectra, the light emitting diode spectrum and the exciton emission data. For the absorption spectra and the exciton spectra you can label these according to their trace color seen in the vials.

Use the background spectrum and the four spectra obtained under the section “Absorption Spectra” to calculate the absorption spectrum for each vial of quantum dots. Plot the absorbance spectrum for each of the vials of quantum dots using the calibrated wavelength scale and include in your report.

For the data obtained under the section “Emission Spectra” first make a plot of the emission spectrum of the blue light emitting diode using the calibrated wavelength scale. Plot the emission spectrum for each of the vials of quantum dots of quantum dots using the calibrated wavelength scale and include in your report.

For the exciton emission spectra, find the wavelength of the maximum emission for each of the vials. Use Equation (14) to calculate the radius of the four sizes of quantum dots. Summarize your results in a Table such as the following.

Solution Color	Peak Wavelength (nm)	Radius (nm)
Color	###.#	#.###

Make a plot of quantum dot radius (y-axis) as a function of the peak wavelength of the emitted light (x-axis).

In the discussion and conclusions section consider the following. (1) What happens to the wavelength of light emitted as the radius of the quantum dot increases? (2) Examine the absorption spectra. From the absorption spectra discuss why a blue light emitting diode creates an exciton and why the red light emitting diode does not for the quantum dots used in this experiment.

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1.18: Kinetics of Hydrogen Peroxide Decomposition

CHEM 174 Physical Chemistry Laboratory II

Hydrogen Peroxide Decomposition

Introduction

The composition of our world is controlled by detailed chemical mechanisms and their rates. Extremely complex mechanisms determine the characteristics of everything from living cells to the atmosphere. For example, chemists are creating mechanisms for the reactions of organic compounds in the polluted urban atmosphere that include almost two million elementary reactions. The goal of chemical kinetics is to better understand the mechanisms and rates of chemical reactions. In this laboratory you will learn some methods that can be applied to understand the mechanisms of many kinds of reactions.

Hydrogen peroxide is an oxidant that is ubiquitous in the environment that is formed by atmospheric processes (Stockwell et al., 1997). Hydrogen peroxide is injurious to cells because it attacks unsaturated fatty acids (lipids) found in cell membranes and consequently cells produce a powerful catalyst, catalase, that decomposes H_2O_2 (Keusch). Catalase is a catalyst (rather than just another reactant) because it reacts both as an electron donor and as an electron acceptor. Catalase is an example of an enzyme, a biological catalyst.

There are many other compounds that decompose hydrogen peroxide such as iodide ion under acidic conditions. The decomposition is characterized by the stoichiometric reaction [1.18.1](#).



If the solution is relatively acidic (with a pH is less than about 3) the rate of reaction [1.18.1](#) is independent of the pH. Assume that the rate of the reaction under acidic conditions is given by Equation [1.18.2](#).

$$Rate = k [I^-]^a [H_2O_2]^b \quad (1.18.2)$$

where k is the rate coefficient, $[I^-]$ is the iodide concentration, $[H_2O_2]$ is the hydrogen peroxide concentration and a and b are the order of the reaction with respect to iodide and hydrogen peroxide, respectively. We will learn something about kinetics by experimentally determining a and b and by estimating k as a pseudo rate coefficient. This laboratory is based on a similar experiment (Hutton, 1968).

Measuring the order of the reaction with respect to the iodide and hydrogen concentrations, “a” and “b”

We could mix many different concentrations of iodide and hydrogen peroxide and measure the rate but the data analysis would be very difficult and confusing. Suppose that we measured the rate using some baseline concentrations of iodide and hydrogen peroxide, $[I^-]_o$ and $[H_2O_2]_o$ respectively. The baseline rate will be called $Rate_o$ as in equation (3).

$$Rate_o = k [I^-]_o^a [H_2O_2]_o^b \quad (1.18.3)$$

constant at $[H_2O_2]_o$. The ratio between the new rate and the baseline rate is give by equation [1.18.4](#).

$$\frac{Rate}{Rate_o} = \frac{k [I^-]^a [H_2O_2]_o^b}{k [I^-]_o^a [H_2O_2]_o^b} \quad (1.18.4)$$

Equation [1.18.4](#) simplifies to equation [1.18.5](#).

$$\frac{Rate}{Rate_o} = \left(\frac{[I^-]}{[I^-]_o} \right)^a \quad (1.18.5)$$

A typical experimental “trick” is to find a way of linearizing the experiment so that its’ results can be fit by a straight line as given by equation (6).

$$y = slope \cdot x + constant \quad (1.18.6)$$

where y in the dependent variable and x is the independent value. In this case linear regression can be used to determine an experimental value. We will do that here by taking the natural logarithms of both sides of equation (6).

$$\ln \left(\frac{\text{Rate}}{\text{Rate}_o} \right) = a \ln \left(\frac{[I^-]}{[I^-]_o} \right)$$

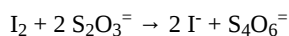
Therefore if we measure the reaction rate at some concentration of iodide and then make several more measurements at differing concentrations of iodide and plot $\ln \left(\frac{\text{Rate}}{\text{Rate}_o} \right)$ as a function of $\ln \left(\frac{[I^-]}{[I^-]_o} \right)$ the slope will be equal to a , the order of the reaction with respect to the iodide concentration.

We can follow similar reasoning to measure b , the order of the reaction with respect to the hydrogen peroxide concentration.

$$\ln \left(\frac{\text{Rate}}{\text{Rate}_o} \right) = b \ln \left(\frac{[H_2O_2]}{[H_2O_2]_o} \right)$$

Measuring the reaction rate

How can the reaction rate of reaction (1) be measured? Thiosulfate ion reacts with iodine to convert it back to iodide as shown in reaction (9) and it does not react to any significant extent with anything else in the solution.



Iodine concentrations remain low as long as there is thiosulfate in the solution. After the thiosulfate is consumed iodine concentrations will increase and in the presence of starch a blue colored complex will form. We can measure the rate of reaction (1) by adding a known amount of a standard sodium thiosulfate solution and some starch to the reacting solution. The time required for the solution to turn blue is measured. The rate is given by equation (10).

$$\text{Rate} = \text{Moles } H_2O_2 \text{ reacted} / \text{Time (s)} = \text{Moles thiosulfate reacted} / \text{Time to turn blue}$$

The formula of sodium thiosulfate is $Na_2S_2O_3$. Sodium thiosulfate may absorb water or react with impurities in solution. Therefore to measure the rate coefficient accurately we should do several different titrations of the sodium thiosulfate solution to accurately establish its' concentration. However we can make estimates by simply assuming the formula to calculate the thiosulfate concentration. This uncertainty does not affect the determination of reaction order at all but it does affect the determination of the rate coefficient.

Estimating a pseudo rate coefficient

We will estimate a pseudo rate coefficient with respect to iodide and another pseudo rate coefficient with respect to hydrogen peroxide.

To estimate a pseudo rate coefficient with respect to iodide, use the data where the iodide was varied and the hydrogen peroxide concentration was kept constant. Under these conditions we may define k' , where $k' = k [H_2O_2]^b$ and the expression for the reaction rate becomes:

$$\text{Rate} = k' [I^-]^a$$

If the measured reaction rate, Rate , is plotted as a function of $[I^-]^a$ then k' can be determined from the slope.

To estimate a pseudo rate coefficient with respect to hydrogen peroxide, use the data where the hydrogen peroxide was varied and the iodide concentration was kept constant. Define this pseudo rate coefficient, k'' , as $k'' = k [I^-]^a$ and the expression for the reaction rate becomes:

$$\text{Rate} = k'' [H_2O_2]^b$$

If the measured reaction rate, Rate , is plotted as a function of $[H_2O_2]^b$ then k'' can be determined from the slope.

Temperature Dependence of Rate Coefficients

The temperature dependence of rate coefficients for many reactions is given by the Arrhenius equation:

$$k = A \exp \left(\frac{-E_a}{RT} \right)$$

where A is the preexponential factor, E_a is the activation energy, R is the ideal gas constant and T is the temperature. In applying this equation be certain the units of E_a and R are consistent. Substituting the Arrhenius equation into the general rate equation for the reaction of hydrogen peroxide with iodide yields,

$$\text{Rate} = A \exp\left(\frac{-E_a}{RT}\right) \times [I^-]^a [H_2O_2]^b$$

Take the natural logarithm of both sides.

$$\ln(\text{Rate}) = \frac{-E_a}{RT} + \ln(A [I^-]^a [H_2O_2]^b)$$

Therefore if we measure the reaction rate at several temperatures at the same concentration of iodide and hydrogen peroxide and then plot $\ln(\text{Rate})$ as the dependent axis (y-axis) and $\frac{1}{T}$ as the independent axis (x-axis) the slope will be equal to $-\frac{E_a}{R}$.

Procedure Part 1:

Prepare a KI solution with a concentration that is about 0.3 M. Use an analytical balance to accurately weigh 25 g of KI. Use a volumetric flask to dilute to 500 ml. Calculate the concentration.

Prepare a H_2O_2 solution with a concentration that is about 0.1 M. Dissolve about 6 ml of 30% hydrogen peroxide in 500 ml distilled water. You do not need to calculate the concentration.

Prepare a sodium thiosulfate solution with a concentration that is about 0.02 M. $S_2O_3^{2-}$ Use an analytical balance to accurately weigh 1.5 g of $Na_2S_2O_3$. Use a volumetric flask to dilute to 500 ml. Calculate the approximate concentration.

Make a 500 ml buffer solution with 0.5 M of acetic acid and 0.5 M sodium acetate.

To see the colors of the reaction products do the following:

Record your observations as you do the following. Place about 5 ml of the KI solution in a test tube. Add a few drops of the hydrogen peroxide solution.

Divide the mixture of KI and hydrogen peroxide between three test tubes. Label as 1, 2 and 3.

Test tube 1) Keep as a reference.

Test tube 2) Add a couple drops of starch solution.

Test tube 3) Add a couple drops of sodium thiosulfate solution and observe. Add a couple of drops of starch solution and observe again.

Keep these test tubes as a reference as you perform the kinetics measurements.

Table 1. Experimental Solutions for Part 1.

	(1) Distilled Water (ml)	(2) Buffer (ml)	(3) KI Solution (ml)	(4) Starch Solution (ml)	(5) Na ₂ S ₂ O ₃ Solution (ml)	(6) More Distilled Water (ml)	(7) H ₂ O ₂ Solution (ml)
	KI Variation						
A	300	25	5	2	25	To make 475	25
B	300	25	10	2	25	To make 475	25
C	300	25	15	2	25	To make 475	25
D	300	25	20	2	25	To make 475	25
E	300	25	25	2	25	To make 475	25
	H ₂ O ₂ Variation						
E	300	25	25	2	25	To Make 475	25
F	300	25	25	2	25	To Make 450	50
G	300	25	25	2	25	To Make 425	75
H	300	25	25	2	25	To Make 400	100
I	300	25	25	2	25	To Make 375	125

First note the temperature of the solutions and record in your notebook. Mix the solutions 1 – 6 together to make solution A but do not add the hydrogen peroxide. Measure the volumes of the KI and of sodium thiosulfate as accurately as possible. Pour the solution into a 500 ml beaker. Accurately measure the volume of the hydrogen peroxide solution. Mix solution A and the hydrogen peroxide solution and determine the time from mixing until the solution turns to a light blue. Record the time to the nearest second. Repeat for all solutions in Table 1. You do not need to repeat solution E, it is listed in Table 1 to indicate that it is part of both the hydrogen peroxide and potassium iodide variations.

Data Summary Sheet

	Time (Min)	Measured Temperature C°
A		
B		
C		
D		
E		
F		
G		
H		
I		

Part 2 Temperature Variation

Table 2. Experimental Solutions for Temperature Variation. Part 2.

	Temperature C°	Distilled Water (ml)	Buffer (ml)	KI Solution (ml)	Starch Solution (ml)	Na ₂ S ₂ O ₃ Solution (ml)	More Distilled Water (ml)	H ₂ O ₂ Solution (ml)
E1	25	300	25	25	2	25	To make 475	25
E2	30	300	25	25	2	25	To make 475	25
E3	35	300	25	25	2	25	To make 475	25
E4	40	300	25	25	2	25	To Make 475	25
E5	45	300	25	25	2	25	To Make 475	25
E6	50	300	25	25	2	25	To Make 475	25

First perform the experiment at room temperature. Repeat the experiment near 30, 35, 40, 45 and 50 °C. For all measurements mix solutions 1 – 6 together but do not add the hydrogen peroxide. Measure the volumes of the KI and of sodium thiosulfate as accurately as possible. Pour the solution into a 500 ml flask. Either perform at room temperature or place in a water bath to warm to the desired temperature. There will be three warm water baths available. Do not heat the hydrogen peroxide to avoid decomposition.

Accurately measure the volume of the hydrogen peroxide solution. Mix the solution and the hydrogen peroxide solution and determine the time from mixing until the solution turns to a light blue – brown color. Record the time to the nearest second. Record the temperature of the final solution and record in your notebook.

Each group will perform a measurement at room temperature and near 30, 35, 40, 45 and 50 °C (five total measurements per group).

Data Summary Sheet for Part 2.

	Time (Min)	Measured Temperature C°
E1		
E2		
E3		
E4		
E5		
E6		

Calculations and Graphs

In your report organize the results of your calculations in tables and show example calculations.

Iodide variation

Use solution E as the baseline solution. Note that the ratios, $[I^-]/[I^-]_0$, for solutions A – E are 1, 2, 3, 4 and 5, respectively. Calculate the ratio of the measured rates (measured times for the solutions to turn blue ($\text{Rate}/\text{Rate}_0$)). Take the natural logs and plot $\ln([I^-]/[I^-]_0)$ as the

independent variable (x-axis) and plot $\ln(\text{Rate}/\text{Rate}_0)$ as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the order of the reaction with respect to iodide from slope. Also determine the r^2 (shared variance) of the fit.

Hydrogen peroxide variation

Use solution E as the baseline solution. Note that the ratios, $[\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0$, for solutions E – I are 1, 2, 3, 4 and 5, respectively. Calculate the ratio of the measured rates (measured times for the solutions to turn blue ($\text{Rate}/\text{Rate}_0$)). Take the natural logs and plot $\ln([\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0)$ as the independent variable (x-axis) and plot $\ln(\text{Rate}/\text{Rate}_0)$ as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the order of the reaction with respect to hydrogen peroxide from the slope. Also determine the r^2 (shared variance) of the fit.

Estimate the pseudo rate coefficients

For solutions A – E calculate the reaction rate (Rate) in terms of moles of hydrogen peroxide per second and calculate $[\text{I}^-]^a$. Plot $[\text{I}^-]^a$ as the independent variable (x-axis) and plot the Rate as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the pseudo rate coefficient from the slope. Also determine the r^2 (shared variance) of the fit.

For solutions E – I calculate the reaction rate (Rate) in terms of moles of hydrogen peroxide per second and calculate $[\text{H}_2\text{O}_2]^b$. Plot $[\text{H}_2\text{O}_2]^b$ as the independent variable (x-axis) and plot the Rate as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the pseudo rate coefficient from the slope. Also determine the r^2 (shared variance) of the fit.

Temperature Variation

For Part 2 plot the natural logarithm of the reaction time as a function of $1/T$ to determine the activation energy of the rate coefficient. Use Kelvin (K) as your temperature unit.

Report

Structure the report as discussed in class and include a discussion of the following questions in your conclusions section.

1. To determine the reaction order of KI or H_2O_2 why is it not necessary to know the either the initial or actual concentrations of KI or H_2O_2 during the experiment?
2. What are the major uncertainties in the results for the reaction orders? What are the major sources of error for the pseudo rate coefficient. What are the r and shared variance (r^2)?
3. Suggest a reaction mechanism from the data. Can you distinguish between the following two elementary reaction mechanisms on the basis of your data?

	Scheme I	Scheme II
Step 1:	$\text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{H}_3\text{O}_2^+$	$\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{OI}^- + \text{H}_2\text{O}$
Step 2:	$\text{H}_3\text{O}_2^+ + \text{I}^- \rightarrow \text{HOI} + \text{H}_2\text{O}$	$\text{OI}^- + \text{H}^+ \rightarrow \text{HOI}$
Step 3:	$\text{HOI} + \text{I}^- \rightarrow \text{I}_2 + \text{OH}^-$	$\text{HOI} + \text{I}^- \rightarrow \text{I}_2 + \text{OH}^-$
Step 4:	$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$	$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$

4. Why is the ionic strength kept constant?
5. What are the lessons that can be transferred from this laboratory exercise to life sciences research?

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Index

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PCHEM1

- 1.1: Safety Laboratory Exercise
- 1.2: Chemical Literature
- 1.3: Experimental Error and Statistics
- 1.4: Chemical Conceptions and Misconceptions
- 1.5: Numerical Data Analysis
- 1.6: Computation of Thermodynamic Quantities
- 1.7: Equation of State
- 1.8: Heat Capacity Ratios for Gases (C_p/C_v)
- 1.9: Chemical Garden - Introduction to Research

PCHEM2

- 1.10: Blackbody Radiation
- 1.11: Atomic Spectroscopy
- 1.12: UV-Vis Absorption Spectroscopy
- 1.13: Particle in a Box
- 1.14: Fourier Transform Infrared Spectroscopy (FTIR)
- 1.15: Biomaterials- Protein Structure Determination by FTIR Spectroscopy
- 1.16: Biomaterials- Studies of Protein Structure by Computational Quantum Chemistry
- 1.17: Nano-Particles and Quantum Dots
- 1.18: Kinetics of Hydrogen Peroxide Decomposition

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 - Table of Contents - [Undeclared](#)
 - Licensing - [CC BY-NC-SA 4.0](#)
 - 1: New Page - [Undeclared](#)
 - 1.1: Safety Laboratory Exercise - [CC BY-NC-SA 4.0](#)
 - 1.2: Chemical Literature - [CC BY-NC-SA 4.0](#)
 - 1.3: Experimental Error and Statistics - [CC BY-NC-SA 4.0](#)
 - 1.4: Chemical Conceptions and Misconceptions - [CC BY-NC-SA 4.0](#)
 - 1.5: Numerical Data Analysis - [CC BY-NC-SA 4.0](#)
 - 1.6: Computation of Thermodynamic Quantities - [CC BY-NC-SA 4.0](#)
 - 1.7: Equation of State - [CC BY-NC-SA 4.0](#)
 - 1.8: Heat Capacity Ratios for Gases (Cp/Cv) - [CC BY-NC-SA 4.0](#)
 - 1.9: Chemical Garden - Introduction to Research - [CC BY-NC-SA 4.0](#)
 - 1.10: Blackbody Radiation - [CC BY-NC-SA 4.0](#)
 - 1.11: Atomic Spectroscopy - [CC BY-NC-SA 4.0](#)
 - 1.12: UV-Vis Absorption Spectroscopy - [CC BY-NC-SA 4.0](#)
 - 1.13: Particle in a Box - [CC BY-NC-SA 4.0](#)
 - 1.14: Fourier Transform Infrared Spectroscopy (FTIR) - [CC BY-NC-SA 4.0](#)
 - 1.15: Biomaterials- Protein Structure Determination by FTIR Spectroscopy - [CC BY-NC-SA 4.0](#)
 - 1.16: Biomaterials- Studies of Protein Structure by Computational Quantum Chemistry - [CC BY-NC-SA 4.0](#)
 - 1.17: Nano-Particles and Quantum Dots - [CC BY-NC-SA 4.0](#)
 - 1.18: Kinetics of Hydrogen Peroxide Decomposition - [CC BY-NC-SA 4.0](#)
 - Back Matter - [CC BY-NC-SA 4.0](#)
 - Index - [CC BY-NC-SA 4.0](#)
 - Glossary - [CC BY-NC-SA 4.0](#)
 - Detailed Licensing - [CC BY-NC-SA 4.0](#)