CHEM301L: PHYSICAL CHEMISTRY LAB MANUAL



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Physical Chemistry Lab Manual

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1: ORIENTATION TO THIS COURSE

Learning Objectives

By the end of this module, you'll be able to:

1. Access all course details in the syllabus, Canvas site, and this manual. This includes:
   - Finding instructions and resources for experimental modules.
   - Understanding guidelines and due dates for written assignments.
   - Accessing rubrics for every assignment.
   - Knowing where to find course policies and support.
2. Explain the specific policies for this course.
3. Effectively plan and prepare for lab meetings and stay on top of course deadlines.
4. Submit assignments through Canvas.

🎯 **Purpose**: The Orientation Module introduces you to the structure, expectations, and tools used in this course. Before beginning the semester's work, it's important that you understand how this course is organized, how you will communicate your findings, and what is expected of you as a member of a collaborative laboratory team. This module will prepare you to navigate the semester successfully.

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1.1: Pre-Semester Orientation Assignments

📅 **Due:** All items in Part I below must be completed before the first day of class (11:59 pm on the day prior to FDOC). Part II must be completed prior to your first scheduled lab meeting, and Part III should be completed as necessary. Lab meetings start on the first full week of classes.

🕒 **Time:** Plan at least four hours in the weeks prior to the first day of classes (FDOC) to complete Part I of this assignment. Parts II and III will take additional time.

🎯 **Purpose**: These pre-semester assignments are designed to help you start the semester prepared and confident. You will get familiar with the course structure, Canvas site, expectations, and resources.

We're excited to begin the semester with you. Before our first in-person meeting, there are a few essential tasks that will set you up for success. Think of this page as your roadmap—everything you need to complete **before the first lab meeting** is gathered here in one place.

In each module, you'll find a "pre-" page like this one to guide you in preparing for our meetings.

Pre-Semester Assignment

Part I. Get Familiar with Course Tools and Policies
Complete the following written and preparation tasks before our first meeting:

1. Explore the Canvas Site
   - Log into Duke's Canvas platform.
   - Locate the hybrid CHEM310L + CHEM 301L course site.
   - Carefully read the Start Here Module.
   - Find the Course Syllabus (posted on Canvas in the Orientation Module).
   - Browse the Modules, Assignments, and Announcements sections.
2. Complete the Orientation Module
   - Find the Duke Physical Chemistry Lab Manual on Libretexts.
   - Read the full "1: Orientation to CHEM301L" Module in the Lab Manual.
   - Review the Duke Chemistry Safety Manual (linked in Canvas or the Lab Manual).
   - Complete the Orientation Assignment (see syllabus).
     - Access and download the "Orientation Assignment" (at the end of the syllabus) from Canvas.
     - Complete the assignment carefully, following all instructions.
     - Submit your finished version as a PDF on Canvas before the first Dry Lab.
3. Download the full lab manual PDF in case of Canvas or LibreTexts outages.

Part II. Prepare for the First Lab Meeting
The first meeting is a "Dry Lab". You do not need eye protection or lab attire during Dry Lab meetings.

1. Be Ready for to use Google CoLab to complete a group activity in the first Lab Meeting
   - Complete the Pre-Lab Assignment for Module 2.
   - Bring your working (and charged!) computer to the first meeting.

Part III. Review Prerequisite Knowledge
You are expected to begin the course with working knowledge from pre-requisite chemistry, physics, and math courses and their associated labs. This content includes the topics below, though this is not an exhaustive list:

1. **Material from prerequisite Chemistry and Physics course:**
   - General chemical principles, units, and stoichiometry
   - Operation of electronic balances and typical chemistry glassware
   - Organic functional group reactivity

- Equilibrium thermodynamics, reaction kinetics, and chemical equilibrium
- Physical and Mathematical Models that describe properties of atoms and molecules
  - Particle in the box model
  - Harmonic Oscillator model (vibration of bonds)
  - Rigid Rotor model (rotation of molecules)
- Electronic structure of atoms and molecules (Atomic and Molecular Orbital Theory)

2. **Specific material from college-level Math pre-requisites:**
   - Derivatives and partial derivatives
   - Matrices and their operations

Warning: Do not take Physical Chemistry Lab unless you have the appropriate prerequisite courses; click to find the prerequisites for CHEM 301 and CHEM 310 which are also prerequisites for the labs. If you need to brush up on any of these areas, please revisit your prior course notes or request resources from the instructor.

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1.2: Course Overview

👋 Welcome to Physical Chemistry Lab!

This laboratory course complements the undergraduate Physical Chemistry lectures by giving students hands-on experience with instruments, data analysis, computational methods, and scientific reporting central to the field of chemistry. Emphasis is placed on interpreting *real* experimental data and applying core physical chemistry concepts through guided inquiry.

The course is managed through Canvas, which hosts announcements, grading, instructor contact information, and assignment submission portals. The laboratory manual is hosted on LibreTexts and linked within Canvas. Because the manual is continually updated, students should always refer to the live LibreTexts site to access the most current version of each experiment.

Where to find Information about this course

1. **Canvas:** Our course site is on Canvas. All course information is accessible through links on Canvas. All assignments will be submitted electronically on Canvas (using embedded Gradescope submission), and all rubrics are available in the submission portal.
2. **Lab Manual:** The lab manual lives on LibreTexts, and this is where you find pre-lab assignments and procedures for each meeting.
    - **CHEM301L** and **CHEM310L** use the same Lab Manual, but each course covers different modules in the latter half of the semester. Be sure to look out for course-specific instructions and use your syllabus schedule to guide you on what modules and sub-modules you should complete.
    - You can download a copy of the lab manual at any time. Please note that the manual is a "living" document that we update regularly. The latest version is available on LibreTexts. We recommend that you download a pdf copy as a backup for times when you need to work offline. All instructions for operating instruments will be available in lab, but you must have all procedures and plans written in your notebook ahead of time (this is part of your pre-lab assignemnt).
3. **Syllabus:** The syllabus contains additional details and policies that are not provided in the public manuals on LibreTexts, including instructor contact information. The detailed schedule of deadlines and assignments is also in the Syllabus document.

Course Structure

This course is organized into instructional modules, each focused on a major topic or technique in physical chemistry. You will work in collaborative groups to complete each experiment, analyze data, and interpret results. However, you will *write* your assignments independently and all written work submitted for individual scores will be your own.

Assignments include:

- Pre-Lab Assignments – due the day of Lab Meeting by 1:00 PM (25 minutes before each meeting)
- Electronic Laboratory Notebooks (ELNs) – due by the end of each lab meeting.
- Post-Lab Assignments and Reports – due for scoring according to the syllabus schedule.

A detailed breakdown of points in each assignment is available in this google spreadsheet (Click).

Promoting Diversity, Inclusion, and Avoiding Harassment



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All members of this course will foster an environment or listening and considering new ideas from a diverse group, with respect for all participants without regard to gender, race, ethnicity, color, sexual orientation, political orientation, age, religion, national origin, disability, or any other aspect of how we identify ourselves other than as fellow scientists.

There is zero tolerance in this course for any form of harassment or hate speech, during class meetings or outside of scheduled class time, which could include verbal or physical conduct that has the purpose or effect of interfering with anyone else's participation or performance, or of creating an intimidating, hostile, or offensive environment; any such harassment will result in dismissal from the course and will be reported to the college.

Duke University's Institutional Statement of Commitment to Diversity and Inclusion is found here (click):

> *"Duke aspires to create a community built on collaboration, innovation, creativity, and belonging. Our collective success depends on the robust exchange of ideas—an exchange that is best when the rich diversity of our perspectives, backgrounds, and experiences flourishes. To achieve this exchange, it is essential that all members of the community feel secure and welcome, that the contributions of all individuals are respected, and that all voices are heard. All members of our community have a responsibility to uphold these values."*

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1.3: Meetings and Deadlines

Meeting Etiquette (Work well with your team of instructors)

There is a team of instructors to help you, including the course director (a Ph.D. chemist) and several Teaching Assistants (TA's) who are graduate students earning their PhD's in chemistry. One or more TA's will be in the lab with you each day, and one of them will be dedicated to helping you and at least one of your lab-mates to run a given experiment. That dedicated TA will be present during the laboratory to assist you, offer tips, and advice.

Use lab time to work on Notebooks and writing assignments: The TAs are available during the scheduled meeting time, and they are trained to help you in a way that supports your learning. Use the scheduled meeting time to work on your data analysis and consult with your TAs so they can help you during your time with them. Consultation and discussion with TA's should happen *during scheduled lab time* - do not leave lab early just because you have finished the experiment and cleaned up.

Sign in and out of lab: You should always *check in* on the sign-in log with the time of your arrival. When you leave the lab meeting for the day, you must *sign out* and get an instructor to sign your sign-out sheet. The TA will check that you have completed your work, shared your data with the class, and cleaned up your workspace before signing you out.

Email policy: We want you to do well, and we want to help you. So *please* ask for help well before your assignment is due. Questions about chemistry are often difficult and time-consuming to answer in an email, thus in-person conversations are required. Take advantage of lab time, office hours, and open labs hours for content-related questions. Email should be reserved for sharing information related to absence, assignment deadlines, errors found in the course materials, or other administrative business.

If you you send an email, the expected response time is 2 *business days*. Your instructors will not respond to you over the weekend, and may not be available.

"Open Lab" Hours: Open Lab hours are times when you may drop by - these are like office hours, but we'll be in the lab or classroom. Open lab hours are posted on the course syllabus.

Office Hours: We expect you to take full advantage of scheduled lab times and the open lab hours to get the help you need. However, if you have done so and still need additional support, you can access your instructors through office hours. The office hours schedule with your team of instructors is posted in the course syllabus. Some instructors hold office hours only upon request, while others prefer a regularly scheduled meeting time.

A list of TAs with their experiment assignments and office hours is posted on the course syllabus.

LABORATORY SAFETY

This course requires you to understand the potential hazards associated with materials, equipment, and procedures within the chemical laboratory. This knowledge is crucial as it directly impacts the level of risk that you and fellow students may face due to your actions and those of others in the laboratory. You can help to minimize the risks posed by chemical hazards to both yourself and others by taking precautions. We strongly encourage you to consistently prioritize safety in your laboratory work. The following requirements have been established with your safety as the primary consideration:

1. A copy of the Duke Chemistry Department Safety Manual is available on the Chemistry web site. All students will read this manual prior to beginning laboratory work.
2. Safety eyewear is always required in the laboratory space.
    a. You will provide your own pair of safety eyewear to use during every lab period. Safety eye wear can be purchased from the Graduate Chemistry Council (GCC).
    b. If you wear prescription glasses, you should also wear safety eyewear that fits over your prescription glasses.
    c. Contact lenses may be worn in the laboratory in addition to wearing safety glasses.
3. No unauthorized work or experimentation will be allowed in the laboratory. Students must always be supervised by an

instructor while in the laboratory spaces.
4. Protective shoes are required in the laboratory - no bare feet, sandals or open-toe footwear.
5. Consumable items should be kept out of the laboratory at all times. Never eat (including chewing gum), drink, or smoke in the laboratory.
6. Per the chemistry department safety policy, skin must be covered in labs. Long pants or skirts must be worn, as well as clothing that covers your entire torso, shoulders, and arms. We know it can get hot in Durham, so bring extra clothes with you to lab on hot days. Clothing that is not appropriate for lab include shorts, skirts, crop tops, low cut shirts, tank tops, and anything that leaves your skin to be exposed to chemical hazards (see Figure below).
7. Long hair must always be tied back while in the laboratory.
8. Safety Data Sheets (SDS) for every chemical to be used in this laboratory course are available online by googling the name of the chemical and "sds". You will read the SDS for each chemical to be used prior to arriving in lab.
9. Failure to observe safety regulations will result in substantial deduction in the lab grade and may result in ejection from the lab session. Persistent violation of safety regulations will result in permanent expulsion from the lab course.
10. **Solvents and Chemicals will be disposed of properly:** Departmental waste disposal procedures are described in the safety manual. However, you should always consult with an instructor before attempting to dispose of any material.
11. Precautions for individual experiments will be discussed with you by the instructional team and are described in the lab manual.

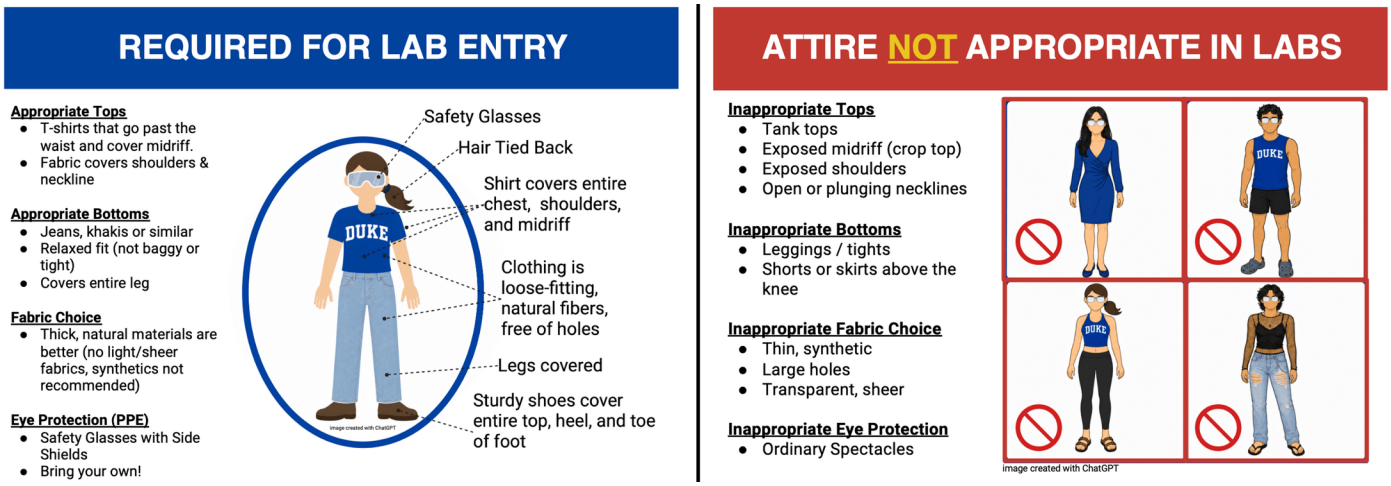


Figure 1.3.1: Figure : Appropriate attire for lab is pictured and described briefly on the left. Inappropriate attire is shown and described on the right. (CC-BY-NC-SA; Kathryn Haas).

Deadlines

Submit your assignments and arrive to meetings on time to receive the maximum points for your work. See the schedule (syllabus) for a detailed schedule of all deadlines.

General Assignment Deadlines

- **Pre-Lab assignments**: Due electronically at 1:00 PM before the lab meeting.
- **Arrival to Lab**: Be ready to begin lab on time at 1:25 pm.
- **ELN (Notebook)**: Due electronically at 6 pm at the end of your scheduled meeting.
- **Post-Experiment assignments**: Due according to the syllabus schedule.
- **Late work**: Final deadline for all work to be graded is 11:59 pm on the last day of classes (LDOC).

Late assignments policy:

- You have one "no-questions asked" Late Token that allows you to hand in any post-lab assignment two weeks past the original deadline. (see below for details)
- Otherwise, the following point deductions will apply:

- Late pre-lab assignments receive zero points, and you may not conduct the experiment if lack of preparation will cause a safety risk or will disrupt the course
- Late reports are deducted 10% for each day (see next page for details), with a maximum penalty of 50%.

Extensions and Late Assignments

This course is designed to keep you on track while also recognizing that real life happens. The policies below aim to balance accountability with flexibility, providing you reasonable options when things don't go as planned.

Policy on Extensions and Late Assignments

General Policy

- Deadlines are essential to ensure that you are prepared for lab work, receive timely feedback, and stay aligned with your team and the instructional schedule.
- Accommodations are always available for students facing serious or ongoing extenuating circumstances. If this applies to you, contact your academic dean to request a formal Dean's Excuse; your Dean will then reach out to your instructors so we can support you appropriately.
- The policies below apply to all students in the absence of a Dean's Excuse.

Late Assignments: If an assignment is not turned in by the deadline, the following point deductions will apply.

- **For Pre-Lab assignments:** Pre-labs are required preparation for all Lab sessions. The policy for pre-labs is the most strict to protect your safety, the safety of expensive equipment, your team's success, and your ability to contribute meaningfully to lab meetings.
  - Pre-labs must be submitted before the lab session begins; they are due at 1:00 PM on the day of your lab meeting.
  - Late pre-labs will receive zero points.
  - If the pre-lab is insufficient or incomplete at the start of lab time, you will not be allowed to participate in the experiment.
- **For All other assignments:** All other assignments can be submitted late but incur a deduction.
  - 10% deduction per 24-hour period, up to a maximum of 50% off.
    Examples:
    - 5 minutes late → 10% off
    - 26 hours late → 20% off
    - More than 5 days late → 50% off
- **Deadline for All Late work**: Late work is only accepted up to 11:59 pm on LDOC (Last Day of Classes).

Extension Token: Each student may use one Extension Token during the semester — no explanation required.

- **The token allows you to submit:**
  - A post-experiment assignment or report up to two weeks late with no penalty, OR
  - Any other assignment up to two weeks late, as long as it doesn't impact safety, team grading, or lab scheduling. (Does not apply to pre-lab assignments)
- ⚠️ **Use It Wisely:**
  - This token is not a substitute for a Dean's Excuse. If you're dealing with a serious situation, ask your Dean or your instructional team for a different level of support.
  - Using the token may delay feedback or grading, which can impact your ability to perform on subsequent assignments. Do not use this as a license to procrastinate!

Final Deadline for Late Work

No late work will be accepted after 11:59 PM on the Last Day of Classes (LDOC).

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1.4: Academic Integrity

Academic Integrity vs Cheating

- **Academic integrity** means your work is an accurate representation of your own learning and understanding.
- **Cheating** or **academic dishonesty** occurs when your work misrepresents what you know, undermining your own learning and the trust that makes meaningful feedback possible.

Why Academic Integrity Matters in this Course

In this course, your written work is both a learning tool and an assessment tool.

- When you write, you articulate and refine your thinking.
- When we read your writing, your instructors and TAs see your reasoning, your decisions, and your conclusions. This allows us to give you feedback you can actually use to grow as a scientist.

You will also give and receive peer feedback. For that feedback to be meaningful — and for you to benefit from it — your work must reflect your own thinking.

Duke Community Standard

All students must adhere to the Duke Community Standard (DCS): Duke University is a community dedicated to scholarship, leadership, and service and to the principles of honesty, fairness, and accountability. Citizens of this community commit to reflect upon these principles in all academic and non-academic endeavors, and to protect and promote a culture of integrity.

To uphold the Duke Community Standard, students agree:

- will not lie, cheat, or steal in my academic endeavors;
- I will conduct myself honorably in all my endeavors;
- I will act if the Standard is compromised.

Regardless of course delivery format, itis the responsibility of all students to understand and follow all Duke policies, including academic integrity(e.g., completing one's own work, following proper citation of sources, adhering to guidance around group work projects, and more). Ignoring these requirements is a violation of the Duke Community Standard. Any questions and/or concerns regarding academic integrity can be directed to the Office of Student Conduct and Community Standards atconduct@duke.edu.

Using AI to Support Your Learning

AI tools (e.g., ChatGPT, Grammarly, Claude) can be powerful learning partners if you use them intentionally and transparently. But, if they are misused, these tools can undermine your learning.

Appropriate use of AI:

AI tools can play a valuable role in your learning process when used intentionally to coach you, or to help improve your writing.
You may use AI applications to:

- Improve organization and structure of your own writing using prompts like "*Revise this paragraph to improve clarity and structure, but keep the original meaning.*"
- Edit for grammar and clarity using prompts like "*Identify grammar errors and suggest fixed without changing the technical*

meaning of my writing."
- Refine your phrasing or writing style. "*Make this explanation appropriate for an audience of scientists outside my specialty.*"
- Brainstorming ways to present an idea you've already developed. "*Suggest alternative ways to phrase this description of my method.*"

After using AI in any of these ways, you must review, edit, and verify the output yourself. Be aware that AI tools can change the meaning of your words, and AI can hallucinate and give test that is not based in reality. You are responsible for ensuring that your final writing is clear, correct, and accurate —and that it represents your own learning, thoughts, and understanding.

Inappropriate use of AI:

Using AI to generate substantive scientific content — such as designing methods, interpreting data, or drafting analysis you have not developed or do not fully understand — is a misuse of these tools.

Examples of inappropriate use of AI:
- Generating new sections or paragraphs you did not develop yourself. (e.g., "Write an introduction section for a scientific manuscript about …")
- Asking AI to analyze your data or draw conclusions that you cannot explain (e.g., "Interpret my results and write the discussion section.")
- Rewriting entire drafts you did not author yourself.
- Fabricating sources, citations, or data.

Misusing AI in this way prevents your instructors and peers from providing meaningful feedback; it prevents you from learning and it wastes everyone's time.

A Quick Test: The "Could I Explain This?" Rule

Before submitting any work that involved AI, ask yourself:

- Could I explain every choice, result, and statement in my own words?
- Could I recreate the reasoning or analysis without AI's help?

If the answer is "no," then the AI use is likely inappropriate for this course.

When in Doubt, ask.

If you are ever unsure about whether an AI tool is supporting your learning appropriately, please ask a member of the instructional team. We are here to help you learn how to use these tools thoughtfully, responsibly, and always in service of your authentic growth as a scientist and writer.

Acknowledgements

Whenever you receive outside help—whether from a friend, a textbook, or an AI tool—you must acknowledge it. To help your instructors understand what kinds of support you are using and where you may need additional guidance, we ask that you clearly document all sources of assistance for each assignment.

Example of an Acknowledgements statement:

This statement on the responsible use of AI tools was created by Kathryn Haas for Advanced Lab Courses at Duke University. The statement was drafted with the support of OpenAI's ChatGPT. It draws inspiration from "AI with Intention: Principles and Action Steps for Teachers and School Leaders" by Tony Frontier and includes insights generously shared by Dr. Eliana Schonberg (Thompson Writing Program at Duke University).

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1.5: Lab Citizenship

In this laboratory course, we conduct ourselves in a safe, inclusive, and respectful manner. A portion of the total available points for this course are allotted to your performance and professional conduct in lab. This includes an expectation for preparation before the lab period, arriving on time, using time effectively, performing the tasks well, contributing to the culture of safety, contributing to the culture of learning, and helping to maintain a clean and safe environment. Your performance and professionalism in the lab is assessed through **Lab Citizenship points**.

🌟What does it mean to be a "Good Lab Citizen"?

Lab Citizenship refers to more than just following rules. It means self-regulating your behavior in a way that supports a safe, respectful, and productive lab environment—without needing constant reminders from instructors.

Your instructors are here to support your learning, not to act as the "lab police." We expect that you will take ownership of your space, your preparation, and your conduct. This includes not just compliance with safety policies, but also contributing positively to the shared environment, being considerate of others, and acting professionally.

Good Lab citizens:

- Arrive on time and ready to work
- Wear proper lab attire and PPE at all times without reminders
- Turn notifications off on electronic devices used during meetings
- Clean up after themselves and leave shared spaces better than they found them
- Use lab time effectively and help their group stay on track
- Label solutions, handle chemicals safely, and follow disposal protocols
- Respect the physical space, equipment, and people in the lab

When you do these things consistently, it frees your instructors to focus on helping you learn and grow as scientists — not on enforcing rules. Your Lab Citizenship grade score reflects your ability to self-regulate and contribute to a positive lab culture.

Lab Citizenship Checklist

Each Wet Lab session, you can earn 1 Lab Citizenship point by demonstrating professional, safe, and respectful lab conduct. This point is awarded as an “all-or-nothing” score based on the following expectations.



⚠️ Students **will not receive partial credit**—failure to meet any of these expectations may result in 0 points for the day.
*Distraction by electronic devices (messages, social media) during lab time is considered a violation of safety and using time well. You are advised to turn off notifications on electronic devices used during meetings.

Lab Citizenship Penalties

While Lab Citizenship is typically graded on a 1-point-per-session basis, certain behaviors may result in point deductions from your lab report score. These behaviors compromise safety, professionalism, or lab functionality and require stronger consequences.

Repeated or serious infractions will result in direct point deductions from your lab report grade for the corresponding module. The instructional team will notify you if a deduction has been applied and explain why. Some, but not all, examples are shown below:



⚠️ Repeated issues (e.g. forgetting goggles, being late, or poor cleanup) may also trigger **a conversation with the instructional team or department administrators** to resolve concerns and may result in failure of the course.

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1.6: ASSIGNMENT DETAILS

Pre-Lab Assignments (Your own work)

Pre-lab assignments must be your own work. To prepare for lab, you should do the following:

Prepare by Wearing Protective Clothing and Bringing Your Protective Eyewear: Arrive dressed appropriately for a laboratory environment. You must bring your own pair of protective eyewear with you, and you must wear them the entire time you are in lab. Safety eye wear can be purchased from the Graduate Chemistry Council (GCC). If lab attire is a problem for the rest of your day, please purchase a lab coat and/or bring a change of clothing with you so that you can cover up in lab. No student should be in lab without wearing protective eyewear and appropriate protective clothing.

Completing the Pre-Lab Assignment: It is absolutely essential that each student be prepared for lab meetings by reading the appropriate module in this manual, and completing the specified pre-laboratory assignments. The pre-laboratory assignments are designed to prepare you to operate efficiently and safely during the experimental module. You will not be allowed to participate in the lab meeting if the pre-lab assignment is not completed before your lab meeting. If there is an extenuating circumstance that prevents your preparation, please inform your instructors as soon as possible.

The pre-lab assignment must be submitted as a single pdf document on Canvas at least 25 minutes before the scheduled lab meeting. Pre-lab assignments should be typed, or at least legible. If you prefer to write out equations by hand, they must be neat and inserted as an image in the appropriate place (please note that handwritten equations are only accepted for pre-lab assignments and ELNs, *but not for post-lab assignments or reports*). If you need advice for how to insert equations or images into your documents, please ask for help at least 48 hours before the assignment is due; an in-person (or zoom) meeting is most appropriate for this issue.

Late pre-laboratory assignments will receive a score of zero, and may prevent you from participating in the laboratory experiences. The pre-lab assignment will be discussed in groups at the beginning of each meeting to support your understanding of the exercises. Your preparedness will be evaluated by your answers to oral questions pertaining to the laboratory from the TA and other lab instructors. The pre-lab and preparation accounts for 5 points of each experiment requiring a pre-lab.

For every experimental module there is a general pre-lab assignment and a specific pre-lab assignment.

General Pre-Lab Assignment (same for all modules)

A template file for preparing your pre-lab assignment is available in your Google Classroom Assignments.

Read the module in canvas and in the lab manual, follow the instructions within, then write a brief **introduction** to the experiment and an **experimental plan** using the following outline:

I. **Description of the Experiment:** In your own words, briefly introduce the topic, describe the theory upon which the experiment is based, and state the goals for this experiment. Keep it concise; lengthy discussions or derivations of equations are unnecessary.
   a. Background (importance/relevance): A brief description and justification of the importance of the topic, *with at least two references to source material* (do not use the lab manual as a reference). Describe the topic, and describe why is it interesting, important, and worth your time to learn.
   b. Theory: A concise paragraph or more describing the general theory for the method/technique used; this section should contain a reference to the appropriate pages of the textbook, or other source material from the literature.
   c. Goals/Purpose: Brief statement of purpose, which should indicate what is analyzed and the technique used. Limit to three to five sentences.

II. **Experimental Plan:** a short summary of the specific things that you would need to know in order to do the experiment without having access to your lab manual, with the understanding that you will always have a TA available to teach you how to use the instrument.

    The best way to approach this task is to thoroughly read the procedure for the experiment. While reading, take notes

on the specifics of the work. What chemicals will you use? If you have to make solutions, what solutions do you need to make and of what concentration? How will you prepare them? What instrument will you use, and what specific instrument settings will you need to input (sometimes you will find this information in the Appendices that discuss the use of the instruments)? How many runs of each sample will you do; and over what wavelength, or temperature, etc. range? You do not need to write down how to use the instrument; we will teach you that. Bottom Line: we want you to write down only that pertinent information about samples, sample preparation, instrument and instrument parameters, numbers of runs, and other things, that you will need to know in order to do your work.

Specific Pre-Lab Assignment

Each module has a pre-lab assignment on the first page of the module. In general, each pre-lab assignment requires you read the entire module and write out the specified pre-lab assignments in your notebook before starting that laboratory work.

Electronic Laboratory Notebooks (ELNs, Group work)

Warning: Use cloud storage and backup

As you save your documents and develop systems of organizing your academic life, please learn to use a cloud server to automatically save and back up your work. Duke University supports cloud storage through Box and Microsoft tools. We will use Google tools in this course because they are the best option to use for collaboration. Proper use of these tools is expected. Please ask Dr. Haas if you need some instruction or recommendations for using these cloud-based tools to avoid loosing your work if/when computer hardware is lost or fails.

While we are aware that there are limited computer labs on campus, you have access to computers in the P-chem lab classroom at any time. Please plan to always complete your work 48 hours in advance so that any issues with your personal devices do not interfere with timely submission of assignments.

Using the electronic laboratory notebook (ELN) template (Group work)

You will complete each experiment in a small group (~3 students), and there will be a dedicated instructor to answer questions. You will record observations using an electronic laboratory notebook (ELN). Templates for each ELN will be provided on Google Docs so that all group members can collaborate on the record keeping. The ELN template is provided as a guide to help you understand the minimum expectation for what should be recorded during the laboratory session. The "Observations and Raw Data" should be edited during lab while your group is working together. You should record all additional information and observations that you think is relevant.

To use the ELN template, one member of the group should create a shared version of the ELN that will be used during the laboratory period, and in which all group members can contribute to the *Observations and Data* section. Then, each group member should make their own "protected" copy, and then complete the post-lab assignment sections with their own work. ***To guard against the possibility of plagiarism, do not share an electronic copy of any ELN that contains your own work on post-lab assignments.***

Group Work in Notebook Keeping (ELN's): Record all observations and primary data as a group. This should include the actual procedure, instrument used, instrument tolerance (error), instrument settings, any notable observations, and all data collected during the lab period. Each group member should collect a copy of the group data and store it in their own files. Every P-chem lab computer has internet access, and you may either email data to yourself, save it using OneDrive, Google Drive, or Box, or collect it using a usb drive. The completed ELN must be submitted for grading before the end of the lab meeting.

The ELN should contain only the information, observations, and data collected while in the laboratory. It should not contain your evaluation the data/observations in any way (that is the post-experiment work). If data are being collected by hand (handwritten on paper) it should be in clear, easy to read format. This handwritten data should be *immediately* entered into a shared ELN file. For data that are collected by a computer interface to your equipment, note the specific name of the data file in case you have to retrieve the file later! Take screen shots as necessary to capture important data to insert into the ELN. Write observations for

each run, including "bad" or aborted runs, in a narrative style and state where the actual data file can be found (including filename) when needed.

Post-Experiment Assignments: (Your own work)

The Post-Lab Assignments (Post-Lab Reflections, Questions, and Reports) must be your individual work. All students will perform data analysis individually, and submit their own work for these assignments. While you should help each other and compare and discuss your process and results within your group, and between groups, each student must complete the data processing and data analysis work for the Post-Lab assignments to earn points. The post-lab assignments are due at 1:00 PM on the day of your next laboratory meeting.

Calculations of results and uncertainties: Unless otherwise instructed all calculations of results and uncertainties should be included as part of the post-experiment work. In this course doing so will require the typing of a lot of mathematics. Please remember that you always have the option of writing your calculations out neatly on plain paper and scanning it to make a digital image that can be incorporated into an electronic notebook entry. Mathpix is recommended to help you convert equation images to Latex for insertion into typed documents (use the Free & Educational use option!).

Reflection on and Discussion of results: In this section you truly "think in writing". Reflect on what you have done. Write this section in your own words after the observations are completed. Include charts, graphs (see below), tables or rearranged data and your rambling thoughts. Remember this is not a formal report. You want to be neat and complete, not necessarily a literary star. This section need not be long, but it should contain all pertinent information.

Graphs: Often you will generate graphs from your primary data files. They must be represented in this section of the laboratory notebook. It is not difficult to include digital copies of graphs within the electronic laboratory notebook, but you should remember that such images can easily make the file sizes large and thus difficult to work with. Below is a procedure that will work to include copies of your graphs in the notebook while minimizing the overall size of the resulting file. A reliable way to capture graphs/plots to insert into your lab notebook is to use WinSnap for PC (or screenshot on Mac). Each lab computer has WinSnap installed. You can take a screen shot by pressing SHIFT + COMMAND + S on the keyboard. This will allow you to select a region for capture and the image will be saved to the clipboard. Press CONTROL + V to paste. You can also open the WinSnap program from the desktop shortcut instead of using keyboard shortcuts. (SAVE OFTEN!)

Reports

CHEM301L includes explicit training in how to write a scientific manuscript *(Don't worry, **310L** friends, you'll get this training in the second semester of P-Chem: 311L)*. Throughout the semester, you will practice writing individual sections (Introduction, Methods, Results, Discussion, Conclusions) as part of your post-lab assignments. These individual sections must be entirely your own work.

At the end of the course, you will apply these skills by writing one full scientific manuscript as a group. Just as professional scientists do, you and your lab partners will collaborate on writing, revising, and integrating your results into a cohesive paper. You will also participate in peer review, giving and receiving feedback to strengthen your manuscript.

Refer to the resources for writing reports here: @WritingforScience

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1.6.1: Rubrics

1.6.2: Old rubrics

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1.6.1: Rubrics

The points that you earn during the semester will determine what letter grade you earn based on a traditional seven-point college grading scale.

$$\text{Letter Grade} \equiv \frac{\text{Points Earned}}{\text{Total Possible Points Earned}} \times 100 \tag{1.6.1.1}$$

Each of the modules and their components are allotted points based on the tentative information below. Teaching assistants will modify the point breakdown as necessary. These rubrics, and all changes to these rubrics, will be applied equally across all student's work in a given semester.

Overall points

Item	Point Breakdown	Total Points
Pre-semester Orientation Assignment	15	15
MatLab Pre-Lab MatLab In-Class Participation	10 25	35
Treatment of Error Pre-Lab Participation during In-Class Problem Session Accurate and Complete Problem Set	10 5 25	40
Absorption Spectra of Dyes Pre-Lab Absorption Spectra of Dyes ELN (including participation)	10 30	40
Rotovibrational Spectroscopy (FTIR) Pre-Lab Rotovibrational Spectroscopy (FTIR) ELN (including participation)	10 30	40
Kinetics Pre-Lab I Kinetics ELN I	10 30	40
Kinetics Pre-Lab II Kinetics ELN II	10 30	40
Writing, Zotero Report Lit Scavenger Hunts Drafts	5 10 10	25
Written Report	50	50
TOTAL		**325**

ELN Point Deductions and other penalties for repeated issues

Issue	Typical deduction
Tardy by between 7 - 15 minutes	- 5 points to ELN *or* is not allowed not participate
Tardy by 16 - 20 minutes	- 10 points to ELN *or* is not allowed not participate
Tardy by more than 20 minutes	- 15 points *and* is not allowed to participate
Failure to wear safety eyewear in lab	- 5 points for each occur ance after first warning
Failure to dress appropriately to lab and must borrow clothing from instructors	- 10 points from ELN for each occurrence, or not allowed to participate
Displaying symptoms of illness and failing to wear a face mask during meetings	- 5 points for each occurrence

Detailed Rubrics for each module

MatLab

Introduction to MatLab	
10 points	Preparation for meeting by installing MatLab on computer, completing Matlab basics tutorials, brining working computer with MatLab installed to lab meeting.
25 points	Participation in the MatLab Tutorial and correct completion of assignment.

Error

Treatment of Experimental Error	
10 points	Preparation for meeting by submission of attempt of all problems.
5 points	Participation in the Error study hall session
25 points	Correct response on all questions

Dyes

Absorption spectra of conjugated Dyes	
10 points	preparation for lab (pre-lab assignment)
5 points	Spectra of the following: Validation of instrument, 4 dyes. Data: Uncertainty in peak wavelengths, comparison with literature values (See Q1-3)
5 points	Calculation of experimental Energy in eV from Λ_max (See Q4)
4 points	Selection of Γ using Matlab "dye" script (3 pts) and explanation of how dye script works (1 pt). (See Q5)
6 points	Calculate Λ_{max} from particle in the box model and compare with experimental value. (See Q6-7)
5 points	Discussion of results. (See Q8)
5 points	Calculation of Λ_{max} and Energy in eV for octatetraene. (See Q9)

FTIR of HCl

Rotovibrational spectroscopy of HCl/DCl using FTIR	
10 points	Preparation for meeting by submission of attempt of all problems.
2 points	Experimental description sufficient to repeat work
1 point	Computational results (simulated spectrum, frequency, and calculated bond length)
1 point	Full Range Background and HCl spectrum

Rotovibrational spectroscopy of HCl/DCl using FTIR	
1 point	Enlarged spectrum at 8 cm resolution with labeled P and Q branches and peak frequencies
1.5 points	Table of peaks and peaks frequencies with J", J', and m values
6 points	Isolated Model: plot of frequency vs m | plot of residuals vs m | Table of derivde parameters and errors
6 points	Coupled Model: plot of frequency vs m | plot of residuals vs m | Table of derived parameters and errors
2 points	Spectrum at three additional resolutions
4.5 points	Discussion (all discussion points addressed correctly and appropriately)
5 points	Post-experiment questions (addressed correctly and appropriately)

How should Apples be prepared for a fruit salad? (Kinetics)

How Should Apples be Prepared for a Fruit Salad?	
10 points	Pre-Lab Assignment Part 1
10 points	Pre-Lab Assignment Part 2
6 points	Materials and Experimental Methods (Inclusive of Parts 1 and 2)
6 point	Part 1A Tables, Figures, and Results
4 points	Part 1A "Thinking about the data"
6 points	Part 1B Tables, Figures, and Results
8 points	Part 1 B "Thinking about the data"
6 points	Part 2A Tables, Figures, and Results
2 points	Part 2A "Thinking about the data"
12 points	Part 2B Tables, Figures, and Results (Pre-experiment questions, prediction of abs vs time data, table of runs, absorbance vs time results plot, M-M plot, L-B plot)
2 points	Part 2B "Thinking about the Data" (What is the mostly likely type of inhibitor, with justification)
8 point	Post-Lab Questions (2 points per question)

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1.6.2: Old rubrics

Calorimetry / Thermochemistry

Students will participate in only one calorimetry experiment.

Solution Calorimetry	
10 points	preparation for lab (pre-lab assignment)
4 points	Extraction of ΔT from thermograms
1 point	Compare manually-calculated ΔT to temperature rise from instrument report.
2 points	Calculation of C_p' for calorimeter
3 points	(1 point for each) Three ΔH_{T1}
3 points	(1 point for each) Three ΔH_{298}
4 pts	Propagation of error (See Q1)
2 pts	Discussion of heats of solution and comparison with literature values. (See Q2)
1 point	Explain the significance of the sign of ΔT_c. (See Q3)
3 points	Hess's law diagram and discussion (See Q4)
3 points	Calculate energy of hydration and lattice energy of sodium acetate trihydrate and dicuss appropriately. (See Q5)
3 points	Analysis f KCl vs NaCl and discussion (See Q6)
1 point	Discussion and explanation about dilute conditions. (See Q7)

Bomb Calorimetry	
10 points	preparation for lab (pre-lab assignment)
3 points	Extraction of ΔT from thermograms
2 point	Compare manually-calculated ΔT to temperature rise from instrument report.
3 points	Calculation of C_v for calorimeter
3 points	Calculation of Δ_{T1} (sugar) (see Q 14)
3 points	str and rxn (see Q 15)
4 points	Compare ΔH_{T1} (sugar) to literature value and discuss. (see Q 16)
4 points	ΔH_f (sugar) (see Q 17)
5 points	Propagation of error and reporting of uncertainties (see Q 18)
3 points	Comparison of different sugars and discussion (see Q 19)

Kinetics

Enzyme Kinetics	
10 points	preparation for lab (pre-lab assignment)
2 points	Show spectra and explain choice of wavelength.
3 points	Absorbance vs time plots; VV_t vs time plots; least squares analysis with error in slope and intercept

Enzyme Kinetics	
3 points	Median velocities, nonlinear and L-B plot
2 points	Choice plot: H-W or E-H
3 points	K_M and V_{max}
3 points	k_2
3 points	Propogation of error and uncertainties (Q1)
2 points	Q2
2 points	Q3
5 points	Q4
2 points	Q5

FTIR of HCl + DCl

Rotovibrational spectroscopy of HCl/DCl using FTIR	
10 points	Preparation for meeting by submission of attempt of all problems.
1 point	Spectra of HCl & DCl - assignments labeled; list of peaks (see Step 1)
4 points	Plot of $\tilde{\nu}_{(m)}$ vs m for 4 isotopes (see Steps 2 & 3)
8 points	$B_e, \alpha_e, \tilde{\nu}_o, I_e, r_e$, and k for each isotope (see Steps 4-8)
4 points	Comparison with literature value (1 points); parts a-c (3 points) (see Step/Q 9)
2 points	Ratios $\frac{\tilde{\nu}_o^*}{\tilde{\nu}_o}$ and $\frac{B_e^*}{B_e}$ for H, D, and $^{35}\mathrm{Cl}$ and $^{37}\mathrm{Cl}$ (see Step 10)
2 points	Explanation of why the ^{35}Cl /^{37}Cl isotope effect so much larger in DCl than it is in HCl (see Step/Q 11)
2 points	Application of Boltzmann populations of the ground-state levels to explain relative band intensities (see Step/Q 12)
2 points	Determination of relative abundance (see Step/Q 13)
4 points	Uncertainty in $B_e, \alpha_e, \tilde{\nu}_o, I_e, r_e$, and k for one isotope (see Step/Q 14)
1 point	Explanation of why we purge the FTIR spectrometer, and why we are careful to purge background and sample similarly (see Step/Q 15)

Computational

Electronic Structure Calculations with Spartan	
2 point	Exercise I: Table summarizing HCl and DCl calculations
1 point	Exercise I: Comparison of computational results to experiment and literature data
1 point	Exercise I: Conclusions about the accuracy of the Hartree-Fock calculation

Electronic Structure Calculations with Spartan	
1 point	Exercise I: Analysis of bond lengths for HCl and DCl
2 point	Exercise II: C-O and C-H bond lengths; CHC and HCO bond angles
1 points	Exercise II: Comparison with literature
2 points	Exercise II: Calculation of energy difference between HOMO and LUMO
2 points	Exercise II: Images and descriptions of HOMO, LUMO, and other orbitals
3 points	Exercise III: Completed table
2 points	Exercise III: Comparison of computational results to literature
1 point	Exercise III: Evaluation of different theories/basis sets
2 points	Exercise IV: Completed table
2 points	Exercise IV: Comparison of computational λ_{max} to experimental and theoretical values
3 points	Exercise IV: Questions from Step 9
2 points	Exercise V: Equilibrium geometry energies of initial, transition, and final states
1 points	Exercise V: Reaction profile plots
2 points	Exercise V: Calculation of activation energy and ΔH

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2: INTRODUCTION TO COMPUTATIONAL TOOLS FOR P-CHEM

Learning Objectives

- Define the terms python, Jupyter notebook, and Google CoLab.
- Practice using basic functions in the python language within a Google CoLab Notebook.
- Gain proficiency with python and Google CoLab for data visualization and data analysis.
- Confirm access to ChemCompute.

🎯 **Purpose**: This module will prepare you to use python and Google CoLab so that you can use these tools to complete data visualization and data analysis assignments in this course.

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2.1: Pre-Lab Assignment

2.2: Python, Jupyter Notebooks, and Google CoLab

2.3: Chem Compute for Molecular Electronic Structure Calculations

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2.1: Pre-Lab Assignment

📅 **Due:** This assignment must be completed before 1:00 PM on your first lab meeting day (see syllabus schedule).

🕒 **Time:** Plan at least two hours to complete this assignment. If you run into technical challenges, this will take additional time.

🎯 **Purpose**: Learn to use Python, Jupyter Notebooks, and Google CoLab so that you arrive to our first meeting prepared to complete your first in-class activity.

Pre-Lab assignment for our first meeting

This assumes you have completed the Orientation Module and have enrolled in our Google Classroom.
To prepare for the first laboratory meeting, please do the following prior to the laboratory period:

- Read this entire module - follow the instructions within the module to complete the tasks listed below.
  - Complete and submit the Google CoLab assignment: *A. Introduction to Python and Jupyter Notebooks (in Google CoLab)*.
  - Create an account on ChemCompute
- Bring your working computer to the meeting.
- This session is a "Dry Lab": We will meet in a classroom, thus lab attire is not necessary for this session.

Be sure you complete the assignment above and submit it on Google Classroom before the deadline!

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2.2: Python, Jupyter Notebooks, and Google CoLab

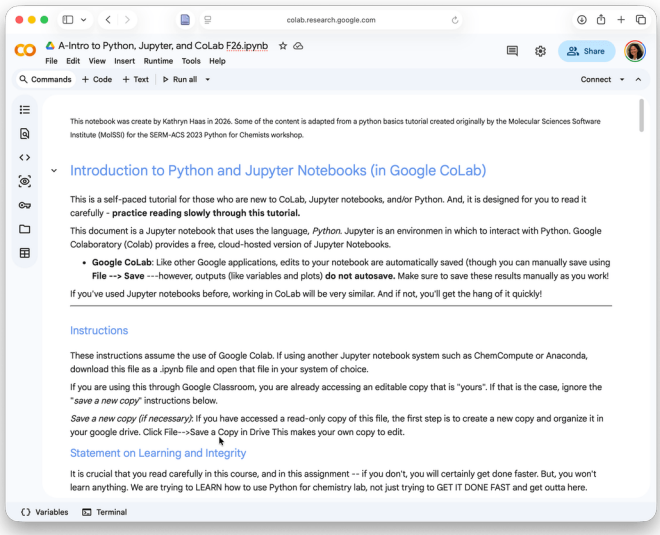
Goal: gain proficiency with python, jupyter notebooks, and Google CoLab so that you can use these tools for data analysis.

Python is a coding language that computers understand. It is more human-friendly when it it done in a Jupyter notebook. And Google CoLab is a free platform for Jupyter Notebooks.

To get started with python, complete the tutorial provided in your google classroom. A link to the "viewable" Google CoLab tutorials are below for anyone outside our course who would like to use it. But, for students enrolled in this course, please go to your Google Classroom and complete the assignments there.

A. **Pre-semester warm up (due before our first meeting):** Intro to Python, Jupyter, and CoLab
B. **Practice with Python for data analysis (we will do this in class)**: Practice with Python In Class

This is a preview of the first tutorial:



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2.3: Chem Compute for Molecular Electronic Structure Calculations

Goal: prepare to use computational tools through the Chem Compute website. We will use them later this semester, but lets get the ball rolling on account set up now.

ChemCompute (https://chemcompute.org/) is a website that gives us free access to molecular electronic structure tools. We will primarily use the GAMESS quantum Chemistry package. To prepare for the semester, sign up for an account using your Duke University credentials.

1. Go to the ChemCompute website (https://chemcompute.org/).
2. Click **Register** in the top left corner (expand the menu in the top left of it is hidden).
3. Choose LOG IN WITH YOUR UNIVERSITY (you must check boxes to indicate that you read and accept the acceptable use policy and indicate that you are not a spy).
4. Use your Duke NetID (the same credentials that you use to log into Duke email) to sign up.

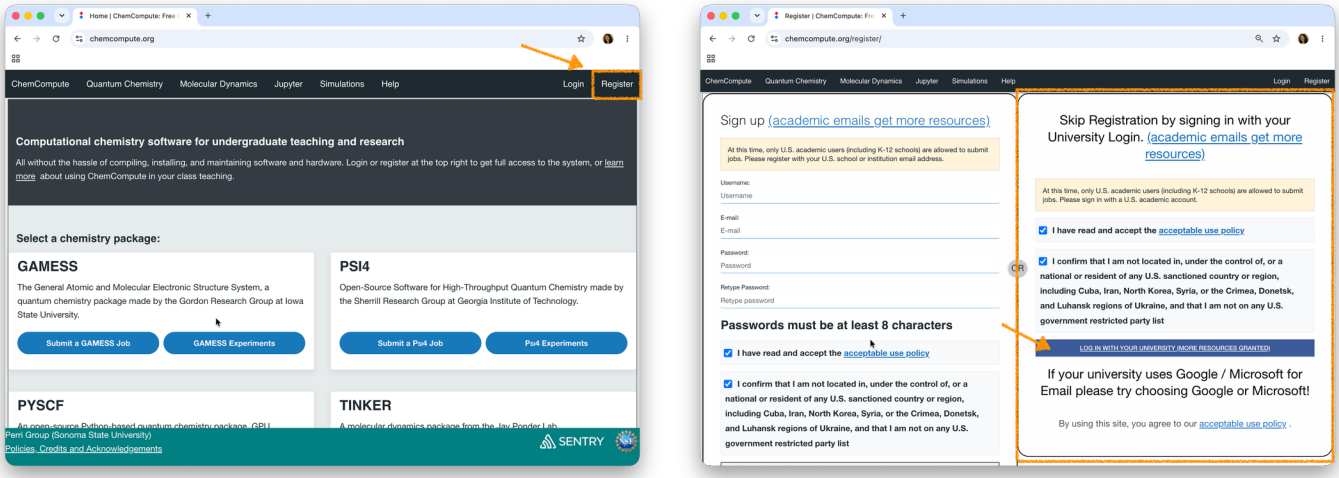


Figure 2.3.1: How to sign up for ChemCompute account using your ".edu" University Credentials. (Kathryn Haas; CC-NC-BY-SA)

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3: THE TREATMENT OF EXPERIMENTAL UNCERTAINTY

Learning Objectives

After completing the readings and practice problems recommended in this module, you should be able to:

- Describe and give examples of the following types of error that effect physical measurements, and identify the types of uncertainties that affect precision and those that affect accuracy.
  - Gross / personal error
  - Systematic error
  - Random error
  - Determinate error
  - Indeterminate error
- Describe strategies for optimizing the accuracy of physical measurements and evaluating the precision of physical measurements.
- Identify the sources of random error in a measurement.
- Propagate uncertainty using mathematics.
- Report values and their uncertainties in the proper form (applying the rules of significant figures to correctly indicate precision).

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3.1: Pre-lab Assignment
3.2: Characterizing Experimental Uncertainty
3.3: Estimating and Reporting Uncertainties (Statistics, Propogation, and Rounding)
3.4: Least Squares Linear Regression
3.5: Rejection of Outliers (Q-test)
3.6: Guidelines for Managing and Reporting Uncertainty in Experiments
3.7: Homework Problems
3.8: References and Additional Reading

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3.1: Pre-lab Assignment

📅 **Due:** The pre-lab assignment must be completed before 1:00 PM on your scheduled lab meeting day (see syllabus schedule).

🕒 **Time:** Two to three hours in class during our first meeting. Plus, plan 4.5 hours outside of class to complete the reading and to attempt the problems in this assignment.

🎯 **Purpose**: This pre-meeting assignment is designed to help you arrive to our next meeting prepared to discuss strategies for estimating uncertainty for different types of experimental results, and for correct reporting of values and their uncertainties. Prepare to participate in the lab meeting by presenting problems on the board, answering questions from your peers, and asking your own questions.

Pre-lab assignment

In preparation for the lab meeting on Error Analysis, please do the following*:

1. **Read this entire module.**
2. **Read D.P. Shoemaker, C.W. Garland and J.W. Nibler, Experiments in Physical Chemistry, 6th Ed., McGraw Hill Co. Inc., New York, 1996, Chapter 2.**
3. **Make a sincere attempt (does not mean you must be correct) for all seven problems** in the problem set; work should be done in a way that you can track your progress and submit your work in electronic form.
4. **Submit record of your work** for all seven problems on Canvas prior to the meeting. Your pre-lab work will be graded based on work shown and evidence of sincere attempt.

Note that the textbooks referenced in this module are available in the Perkins library, and on Canvas in pdf format (or Duke students click here).
We will meet in a classroom, thus lab attire is not necessary for this session.

*For our overachievers and those who want more, recommended additional reading includes: D.A. Skoog, D.M. West, F.J. Holler and S.R. Crouch, Analytical Chemistry: An Introduction, 7th Ed., Saunders College Publishing, New York, 2000, Chapters 5-7.

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3.2: Characterizing Experimental Uncertainty

In this course, you will need to determine the confidence in your results by doing appropriate error analysis. This section and the next are meant to review the types of experimental errors that affect accuracy and precision and to remind you of the simple methods for propagating error.

Errors That Affect Accuracy

Accuracy is how close a measure of central tendency is to its expected value, μ. We express accuracy either as an absolute error, *e*

$$e = \overline{X} - \mu \tag{3.2.1}$$

or as a percent relative error, %*e*

$$\%e = \frac{\overline{X} - \mu}{\mu} \times 100 \tag{3.2.2}$$

Although Equation 3.2.1 and Equation 3.2.2 use the mean as the measure of central tendency, we also can use the median.

> The convention for representing a statistical parameter is to use a Roman letter for a value calculated from experimental data, and a Greek letter for its corresponding expected value. For example, the experimentally determined mean is $\overline{X}$ and its underlying expected value is μ. Likewise, the experimental standard deviation is s and the underlying expected value is σ.

We identify as determinate an error that affects the accuracy of an analysis. Each source of a ***determinate error*** has a specific magnitude and sign. Some sources of determinate error are positive and others are negative, and some are larger in magnitude and others are smaller in magnitude. The cumulative effect of these determinate errors is a net positive or negative error in accuracy.

> It is possible, although unlikely, that the positive and negative determinate errors will offset each other, producing a result with no net error in accuracy.

We assign determinate errors into four categories—sampling errors, method errors, measurement errors, and personal errors—each of which we consider in this section.

Sampling Errors

A determinate sampling error occurs when our sampling strategy does not provide a us with a representative sample. For example, if we monitor the environmental quality of a lake by sampling from a single site near a point source of pollution, such as an outlet for industrial effluent, then our results will be misleading. To determine the mass of a U. S. penny, our strategy for selecting pennies must ensure that we do not include pennies from other countries.

> An awareness of potential sampling errors especially is important when we work with heterogeneous materials. Strategies for obtaining representative samples are covered in Chapter 5 of Harvey's Analytical Chemistry text on LibreTexts.

Method Errors

In any analysis the relationship between the signal, S_{total}, and the absolute amount of analyte, n_A, or the analyte's concentration, C_A, is

$$S_{total} = k_A n_A + S_{mb} \tag{3.2.3}$$

$$S_{total} = k_A C_A + S_{mb} \tag{3.2.4}$$

where k_A is the method's sensitivity for the analyte and S_{mb} is the signal from the method blank. A ***method error*** exists when our value for k_A or for S_{mb} is in error. For example, a method in which S_{total} is the mass of a precipitate assumes that k is defined by a pure precipitate of known stoichiometry. If this assumption is not true, then the resulting determination of n_A or C_A is inaccurate. We can minimize a determinate error in k_A by calibrating the method. A method error due to an interferent in the reagents is minimized by using a proper method blank.

Measurement Errors

The manufacturers of analytical instruments and equipment, such as glassware and balances, usually provide a statement of the item's maximum ***measurement error***, or ***tolerance***. For example, a 10-mL volumetric pipet (Figure 3.2.1) has a tolerance of ±0.02 mL, which means the pipet delivers an actual volume within the range 9.98–10.02 mL at a temperature of 20 °C. Although we express this tolerance as a range, the error is determinate; that is, the pipet's expected volume, μ, is a fixed value within this stated range.

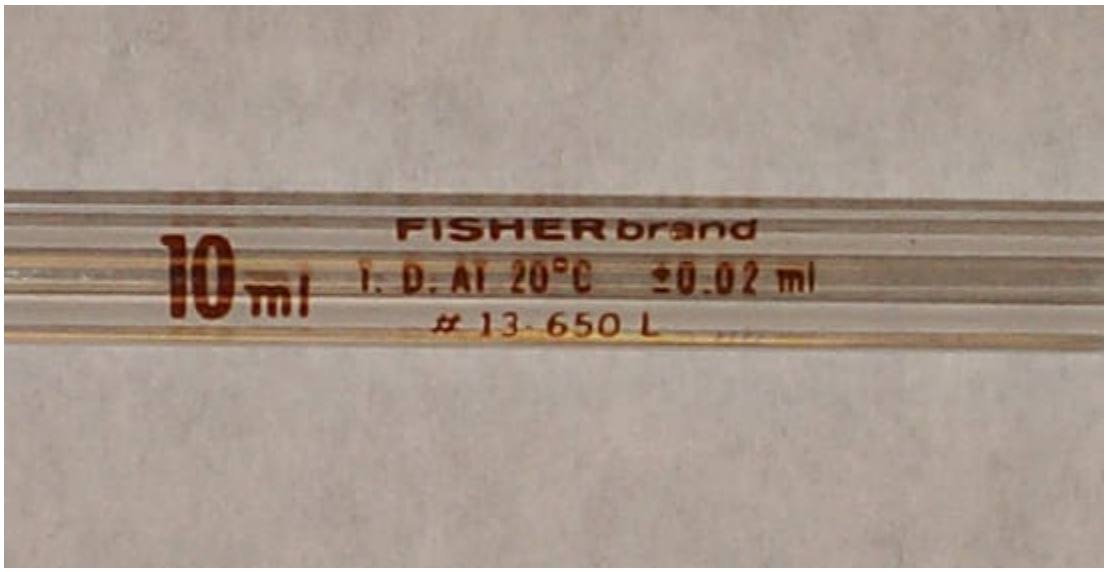


Figure 3.2.1 : Close-up of a 10-mL volumetric pipet showing that it has a tolerance of ±0.02 mL at 20 °C.

Volumetric glassware is categorized into classes based on its relative accuracy. **Class A glassware** is manufactured to comply with tolerances specified by an agency, such as the National Institute of Standards and Technology or the American Society for Testing and Materials. The tolerance level for Class A glassware is small enough that normally we can use it without calibration. The tolerance levels for **Class B glassware** usually are twice that for Class A glassware. In other words, Class B is less accurate. Other types of volumetric glassware, such as beakers and graduated cylinders, are not used to measure volume accurately. Table 3.2.1 provides a summary of typical measurement errors for Class A volumetric glassware. Tolerances for digital pipets and for balances are provided in Table 3.2.2 and Table 3.2.3 .

Tolerance Limits for Class A Volumetric Glassware

*Table 3.2.1 : Measurement Errors for **Class A Volumetric Glassware***

Volumetric Pipets		Volumetric Flasks		Burets	
Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)
1	± 0.006	5	± 0.02	10	± 0.02
2	± 0.006	10	± 0.02	25	± 0.03
5	± 0.01	25	± 0.03	50	± 0.05
10	± 0.02	50	± 0.05		
20	± 0.03	100	± 0.08		
25	± 0.03	250	± 0.12		
50	± 0.05	500	± 0.20		
100	± 0.08	1000	± 0.30		
		2000	± 0.50		

Tolerance limits for Digital Pipettes

Table 3.2.2 : Measurement Errors for Digital Pipets

Pipet Range	Volume (mL or μL)	Percent Measurement Error
10–100 μL	10	$\pm 3.0\%$
	50	$\pm 1.0\%$
	100	$\pm 0.8\%$
100–1000 μL	100	$\pm 3.0\%$
	500	$\pm 1.0\%$
	1000	$\pm 0.6\%$
1–10 mL	1	$\pm 3.0\%$
	5	$\pm 0.8\%$
	10	$\pm 0.6\%$

The tolerance values for the volumetric glassware in Table 3.2.1 are from the ASTM E288, E542, and E694 standards. The measurement errors for the digital pipets in Table 3.2.2 are from www.eppendorf.com.

Tolerance Limits for Some Common Balances

Table 3.2.3 : Measurement Errors for Selected Balances

Balance	Capacity (g)	Measurement Error
Precisa 160M	160	± 1 mg
A & D ER 120M	120	± 0.1 mg
Metler H54	160	± 0.01 mg

We can minimize a determinate measurement error by calibrating our equipment. Balances are calibrated using a reference

weight whose mass we can trace back to the SI standard kilogram. Volumetric glassware and digital pipets are calibrated by determining the mass of water delivered or contained and using the density of water to calculate the actual volume. It is never safe to assume that a calibration does not change during an analysis or over time. One study, for example, found that repeatedly exposing volumetric glassware to higher temperatures during machine washing and oven drying, led to small, but significant changes in the glassware's calibration [Castanheira, I.; Batista, E.; Valente, A.; Dias, G.; Mora, M.; Pinto, L.; Costa, H. S. *Food Control* **2006**, *17*, 719–726]. Many instruments drift out of calibration over time and may require frequent recalibration during an analysis.

Personal Errors

Finally, analytical work is always subject to ***personal error***, examples of which include the ability to see a change in the color of an indicator that signals the endpoint of a titration, biases, such as consistently overestimating or underestimating the value on an instrument's readout scale, failing to calibrate instrumentation, and misinterpreting procedural directions. You can minimize personal errors by taking proper care.

Identifying Determinate Errors

Determinate errors often are difficult to detect. Without knowing the expected value for an analysis, the usual situation in any analysis that matters, we often have nothing to which we can compare our experimental result. Nevertheless, there are strategies we can use to detect determinate errors.

The magnitude of a constant ***determinate error*** is the same for all samples and is more significant when we analyze smaller samples. Analyzing samples of different sizes, therefore, allows us to detect a constant determinate error. For example, consider a quantitative analysis in which we separate the analyte from its matrix and determine its mass. Let's assume the sample is 50.0% w/w analyte. As we see in Table 3.2.4 , the expected amount of analyte in a 0.100 g sample is 0.050 g. If the analysis has a positive constant determinate error of 0.010 g, then analyzing the sample gives 0.060 g of analyte, or an apparent concentration of 60.0% w/w. As we increase the size of the sample the experimental results become closer to the expected result. An upward or downward trend in a graph of the analyte's experimental concentration versus the sample's mass (Figure 3.2.2) is evidence of a constant determinate error.

Table 3.2.4 : Effect of a Constant Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Constant Error (g)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	0.010	0.060	60.0
0.200	0.100	0.010	0.110	55.0
0.400	0.200	0.010	0.210	52.5
0.800	0.400	0.010	0.410	51.2
1.600	0.800	0.010	0.810	50.6

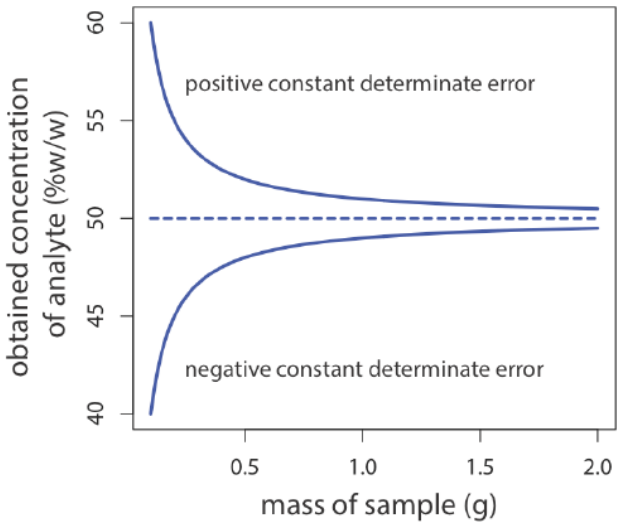


Figure 3.2.2 : Effect of a constant positive determinate error of +0.01 g and a constant negative determinate error of −0.01 g on the determination of an analyte in samples of varying size. The analyte's expected concentration of 50% w/w is shown by the dashed line.

A ***proportional determinate error***, in which the error's magnitude depends on the amount of sample, is more difficult to detect because the result of the analysis is independent of the amount of sample. Table 3.2.5 outlines an example that shows the effect of a positive proportional error of 1.0% on the analysis of a sample that is 50.0% w/w in analyte. Regardless of the sample's size, each analysis gives the same result of 50.5% w/w analyte.

Table 3.2.5 : Effect of a Proportional Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Proportional Error (%)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	1.00	0.0505	50.5
0.200	0.100	1.00	0.101	50.5
0.400	0.200	1.00	0.202	50.5
0.800	0.400	1.00	0.404	50.5
1.600	0.800	1.00	0.808	50.5

One approach for detecting a proportional determinate error is to analyze a standard that contains a known amount of analyte in a matrix similar to our samples. Standards are available from a variety of sources, such as the National Institute of Standards and Technology (where they are called Standard Reference Materials) or the American Society for Testing and Materials. Table 3.2.6 , for example, lists certified values for several analytes in a standard sample of *Gingko biloba* leaves. Another approach is to compare our analysis to an analysis carried out using an independent analytical method that is known to give accurate results. If the two methods give significantly different results, then a determinate error is the likely cause.

Table 3.2.6 : Certified Concentrations for SRM 3246: Gingko bilbo (Leaves)

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
Flavonoids/Ginkgolide B (mass fraction in mg/g)	Qurecetin	2.69 ± 0.31
	Kaempferol	3.02 ± 0.41
	Isorhamnetin	$0.517 \pm 0.0.99$
	Total Aglycones	6.22 ± 0.77
Selected Terpenes (mass fraction in mg/g)	Ginkgolide A	0.57 ± 0.28
	Ginkgolide B	0.470 ± 0.090

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
	Ginkgolide C	0.59 ± 0.22
	Ginkgolide J	0.18 ± 0.10
	Bilobalide	1.52 ± 0.40
	Total Terpene Lactones	3.3 ± 1.1
Selected Toxic Elements (mass fraction in ng/g)	Cadmium	20.8 ± 1.0
	Lead	995 ± 30
	Mercury	23.08 ± 0.17

The primary purpose of this Standard Reference Material is to validate analytical methods for determining flavonoids, terpene lactones, and toxic elements in *Ginkgo biloba* or other materials with a similar matrix. Values are from the official Certificate of Analysis available at www.nist.gov.

Constant and proportional determinate errors have distinctly different sources, which we can define in terms of the relationship between the signal and the moles or concentration of analyte (Equation 3.2.3 and Equation 3.2.4). An invalid method blank, S_{mb}, is a constant determinate error as it adds or subtracts the same value to the signal. A poorly calibrated method, which yields an invalid sensitivity for the analyte, k_A, results in a proportional determinate error.

Errors that Affect Precision

Precision is a measure of the spread of individual measurements or results about a central value, which we express as a range, a standard deviation, or a variance. Here we draw a distinction between two types of precision: repeatability and reproducibility. ***Repeatability*** is the precision when a single analyst completes an analysis in a single session using the same solutions, equipment, and instrumentation. ***Reproducibility***, on the other hand, is the precision under any other set of conditions, including between analysts or between laboratory sessions for a single analyst. Since reproducibility includes additional sources of variability, the reproducibility of an analysis cannot be better than its repeatability.

The ratio of the standard deviation associated with reproducibility to the standard deviation associated with repeatability is called the Horowitz ratio. For a wide variety of analytes in foods, for example, the median Horowtiz ratio is 2.0 with larger values for fatty acids and for trace elements; see Thompson, M.; Wood, R. "The 'Horowitz Ratio'–A Study of the Ratio Between Reproducibility and Repeatability in the Analysis of Foodstuffs," *Anal. Methods*, **2015**, *7*, 375–379.

Errors that affect precision are indeterminate and are characterized by random variations in their magnitude and their direction. Because they are random, positive and negative ***indeterminate errors*** tend to cancel, provided that we make a sufficient number of measurements. In such situations the mean and the median largely are unaffected by the precision of the analysis.

Sources of Indeterminate Error

We can assign indeterminate errors to several sources, including collecting samples, manipulating samples during the analysis, and making measurements. When we collect a sample, for instance, only a small portion of the available material is taken, which increases the chance that small-scale inhomogeneities in the sample will affect repeatability. Individual pennies, for example, may show variations in mass from several sources, including the manufacturing process and the loss of small amounts of metal or the addition of dirt during circulation. These variations are sources of indeterminate sampling errors.

During an analysis there are many opportunities to introduce indeterminate method errors. If our method for determining the mass of a penny includes directions for cleaning them of dirt, then we must be careful to treat each penny in the same way. Cleaning some pennies more vigorously than others might introduce an indeterminate method error.

Finally, all measuring devices are subject to indeterminate measurement errors due to limitations in our ability to read its scale. For example, a buret with scale divisions every 0.1 mL has an inherent indeterminate error of ±0.01–0.03 mL when we estimate the volume to the hundredth of a milliliter (Figure 3.2.3).

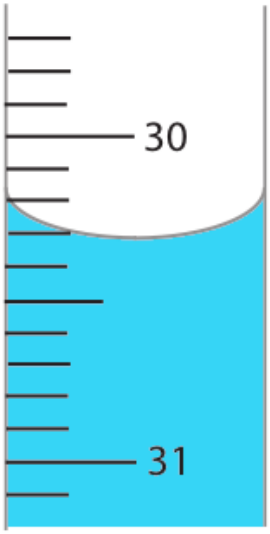


Figure 3.2.3 : Close-up of a buret showing the difficulty in estimating volume. With scale divisions every 0.1 mL it is difficult to read the actual volume to better than ±0.01–0.03 mL.

Evaluating Indeterminate Error

Indeterminate errors associated with our analytical equipment or instrumentation generally are easy to estimate if we measure the standard deviation for several replicate measurements, or if we monitor the signal's fluctuations over time in the absence of analyte (Figure 3.2.4) and calculate the standard deviation. Other sources of indeterminate error, such as treating samples inconsistently, are more difficult to estimate.

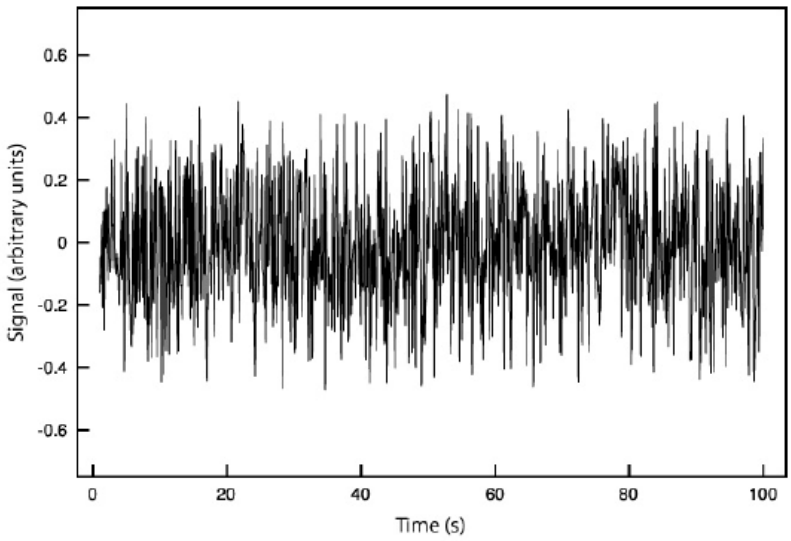


Figure 3.2.4 : Background noise in an instrument showing the random fluctuations in the signal.

Error and Uncertainty

Analytical chemists make a distinction between error and uncertainty [Ellison, S.; Wegscheider, W.; Williams, A. *Anal. Chem.* **1997**,

69, 607A–613A]. ***Error*** is the difference between a single measurement or result and its expected value. In other words, error is a measure of ***bias***. As discussed earlier, we divide errors into determinate and indeterminate sources. Although we can find and correct a source of determinate error, the indeterminate portion of the error remains.

Uncertainty expresses the range of possible values for a measurement or result. Note that this definition of uncertainty is not the same as our definition of precision. We calculate precision from our experimental data and use it to estimate the magnitude of indeterminate errors. Uncertainty accounts for all errors—both determinate and indeterminate—that reasonably might affect a measurement or a result. Although we always try to correct determinate errors before we begin an analysis, the correction itself is subject to uncertainty.

Here is an example to help illustrate the difference between precision and uncertainty. Suppose you purchase a 10-mL Class A pipet from a laboratory supply company and use it without any additional calibration. The pipet's tolerance of ±0.02 mL is its uncertainty because your best estimate of its expected volume is 10.00 mL ± 0.02 mL. This uncertainty primarily is determinate. If you use the pipet to dispense several replicate samples of a solution and determine the volume of each sample, the resulting standard deviation is the pipet's precision. Table 3.2.8 shows results for ten such trials, with a mean of 9.992 mL and a standard deviation of ±0.006 mL. This standard deviation is the precision with which we expect to deliver a solution using a Class A 10-mL pipet. In this case the pipet's published uncertainty of ±0.02 mL is worse than its experimentally determined precision of ±0.006 ml. Interestingly, the data in Table 3.2.8 allows us to calibrate this specific pipet's delivery volume as 9.992 mL. If we use this volume as a better estimate of the pipet's expected volume, then its uncertainty is ±0.006 mL. As expected, calibrating the pipet allows us to decrease its uncertainty [Kadis, R. *Talanta* **2004**, *64*, 167–173].

Table 3.2.8 : Experimental Results for Volume Dispensed by a 10–mL Class A Transfer Pipet

Replicate	Volume (ml)	Replicate	Volume (mL)
1	10.002	6	9.983
2	9.993	7	9.991
3	9.984	8	9.990
4	9.996	9	9.988
5	9.989	10	9.999

Adapted from 4.2: Characterizing Experimental Errors by David Harvey.

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3.3: Estimating and Reporting Uncertainties (Statistics, Propogation, and Rounding)

In many physical chemistry experiments, the goal is to obtain numerical results by taking measurements and calculating averages or applying theoretical formulas. However, simply producing a number isn't enough – it's essential to evaluate its quality. How accurate is the result? Accuracy indicates the level of uncertainty associated with the measurement. Overstating accuracy without proper justification can be misleading, while understating it can undervalue the result and lead to wasted effort and resources.

This page summarizes two main ways to approach the estimation of uncertainty. You will practice when and how to use each strategy by completing the problem set at the end of this module.

1. **Strategy 1: Statistical Analyses** can be used to estimate uncertainty when there are multiple replicates of the same measurement(s).
2. **Strategy 2: Propagation of Uncertainties** can be used to estimate uncertainty when using measured values in a function to calculate another numerical value (the vlaue of the function).

A major goal of this module is for you to learn when and how to apply these equations to perform statistical analysis or propagate uncertainties through a function. This skill will be required in nearly every future module in this course.

A summary of useful information and equations is below.

1. Statistical Analyses (on replicate measurements):

Average or mean: The average (or mean) of N measurements on the variable x is:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{3.3.1}$$

Standard deviation (S) is the spread around the mean of several replicate measurements. It has the same units as the measurement and is commonly used to report uncertainty (see Skoog Ch. 6 p 126)

$$S = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}} \tag{3.3.2}$$

Variance (S^2) is the dispersion between data points. The units are the square of the measured units.

The **Confidence Limits (CL)** are the values that define the confidence interval (which is the bounds about which an experimental value should be located with a given probability). The confidence limit is useful for small sample sizes. A common confidence limit is the 95% confidence limit, and its value is given by the following (see Skoog Ch7 pg 150 and Shoemaker Ch 2 eq 34).

$$CL_{0.95} = t_{0.95}S_m = t_{0.95}\frac{S}{\sqrt{N}} \tag{3.3.3}$$

or more generally

$$CL = \bar{x} \pm \frac{tS}{\sqrt{N}} \tag{3.3.4}$$

where t is the critical t value (from Student's t test) that depends on the degrees of freedom and the given probability. A table of critical t values can be found online. (See also Shoemaker Ch 2, Table 3)

2. Propagation of uncertainties (for values determined from a function):

Note on symbolism

I have chosen to use symbolism that is partly, but not completely, consistent with Shoemaker text. The following symbols are used on this page:

- **Values** are symbolized as x , y, z (these are values that have some uncertainty associated with them).
- The value of a **Function** is symbolized as F.
- **Uncertainty** in the values x, y, z, F are symbolized as u_x, u_y, u_z, u_F, respectively.*
- Coefficients or absolute constants are symbolized by a, b, c.

*u_x is used here to indicate the uncertainty in value x. Shoemaker uses $\Delta(x)$, which is a bit confusing, since it looks a lot like Δx which means "change in x" in many science fields. Ugh... u_x feels better to me, so I use it here.

Using partial derivatives

When using values (x , y, z) to calcuate the value of a function (F), we must propagate uncertainties of each operand (u_x, u_y, u_z,) to determine the uncertainty in the function's value u_F. This is accomplished by taking the square root of the sum of the squares of the partial derivative of the function with respect to each variable (eg partial derivative with respect to x is $\frac{\partial F}{\partial x}$), multiplied by the uncertainty in that variable (eg uncertainty in x is u_x, and the square of the uncertainty is u_x^2. In mathematical form, this is given below (from Shoemaker Ch 2 p 56, eq 54).

$$u_F^2 = \left(\frac{\partial F}{\partial x}\right)^2 u_x^2 + \left(\frac{\partial F}{\partial y}\right)^2 u_y^2 + \left(\frac{\partial F}{\partial z}\right)^2 u_z^2 + \ldots \tag{3.3.5}$$

It is convenient to rearrange this equation as follows to give the uncertainty in the value derived from the function:

$$u_F = \sqrt{\left(\frac{\partial F}{\partial x}\right)^2 u_x^2 + \left(\frac{\partial F}{\partial y}\right)^2 u_y^2 + \left(\frac{\partial F}{\partial z}\right)^2 u_z^2 + \ldots} \tag{3.3.6}$$

Simpler shortcuts:

In some cases, there are shortcuts that allow you to approximate uncertainties without taking the partial derivatives. In the examples below, assume that a, b, c are constants and x , y, z are variables with associated uncertaintyu_x, u_y, u_z:

For functions with only addition and subtraction of values with associated uncertainty (eg $F = ax \pm by \pm cz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 55)

$$u_F = \sqrt{a^2u_x^2 + b^2u_y^2 + c^2u_z^2} \tag{3.3.7}$$

For functions that involve only multiplication and division (eg $F = axyz$ **or** $F = axy/z$ **or** $F = a/xyz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 56)

$$u_F = F\sqrt{\frac{u_x^2}{x^2} + \frac{u_y^2}{y^2} + \frac{u_z^2}{z^2}} \tag{3.3.8}$$

For functions that involve taking a variable to the power of a constant (eg $F = ax^n$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 57)

$$u_F = F\sqrt{n^2\frac{u_x^2}{x^2}} \rightarrow u_F = Fn\frac{u_x}{x} \tag{3.3.9}$$

For functions where a variable is an exponent (eg $F = ae^x$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 58)

$$u_F = \sqrt{a^2e^{2x}u_x^2} \rightarrow u_F = Fu_x \tag{3.3.10}$$

For functions taking the logarithm of a variable (eg $F = a\ln(x)$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 59)

$$u_F = \sqrt{\frac{a^2}{x^2}u_x^2} \rightarrow u_F = a\frac{u_x}{x} \tag{3.3.11}$$

3. Reporting Numeric Results

All numeric results in this course should be reported with explicit statement of uncertainty. The following format is expected:

$$\text{Numeric Value } \pm \text{Uncertainty} \tag{3.3.12}$$

In your written assignments for this course use the following guidelines when reporting a "final" numeric value. You will be required to use your *best judgement* and to provide a *written justification* of your logic for reporting all final values. More detailed information is found below the guidelines and also in the Shoemaker text.

Guidelines for reporting final numerical values:

- Rules for reporting significant figures should be followed.
- The number of useful decimal places in the uncertainty should match the number of decimal places reported in the value.
- The certainty of a numeric value determined from a function cannot be be more than the certainty of its operands.

A summary of rules for reporting significant Figures (from Shoemaker Ch 2)

The following rules apply only for reporting the *final* value, not for intermediate rounding steps during calculation. In general, do not round values during the calculation process if it can be avoided. However, if you must round prior to completing a calculation, then retain *at least one digit more than would be considered "significant"*, and the more the better.

Rules for Rounding Final Values:

Follow the following rules depending on the digit immediately to the right of the place you are rounding. The examples below are rounding to the place underlined, and **the digit immediately to the right is bolded**.

a. Increase the last retained digit by 1 if the nearest dropped digit is more than 5, or if it is 5 followed by any non-zero digits:
   - Examples:
     6.78**9** rounds to 6.79
     54.9**1**23 rounds to 54.9
b. Leave the last retained digit unchanged if the nearest dropped digit is less than 5:
   - Examples:
     2.34**6** rounds to 2.35
     0.212**3** rounds to 0.21
c. If the leftmost digit to be dropped is 5 followed by no digits except zero, then increase the last retained digit by 1 if it is odd, and leave it unchanged if it is even:
   - Examples:
     15.32**5** rounds to 15.32
     15.33**5** rounds to 15.34
d. There are times when you should retain an extra digit so that your reported uncertainty is reasonable.

Rules for tracking significant figures for calculated values

Addition: When adding numeric values, the result's precision is limited by the least precise value involved. The number of decimal places in the result should match the fewest decimal places in any component. For example:

$$\begin{aligned} &15.4 \\ +&2.87 \\ +&7.621 \\ =&25.916 \rightarrow 25.9 \end{aligned} \tag{3.3.13}$$

Subtraction: When subtracting, the result's precision is limited by the least precise value involved, and the precision of the result will always be less than that of the operands. For example:

$$\begin{aligned} &289.461 \\ -&288.58 \\ &0.881 \rightarrow 0.88 \end{aligned} \tag{3.3.14}$$

Let's do an analysis to illustrate what this means. In the example above, let's assume an uncertainty of ± 3 in the rightmost digit of each number. Based on this assumption, the least precise operand has uncertainty of ~ 0.01%, while the final reported value has an uncertainty of 3.4%!

When multiplying and dividing: In multiplication and division, the precision of the result is limited by the least precise number involved. The number of significant figures in the result should align with the component having the fewest. ***Note that relative precision isn't solely dependent on the number of significant figures;*** for instance, 99 with two significant figures is approximately as precise as 101 with three. When unsure, do an analysis of the relative uncertainty, and if the uncertinties are approximately equal, use the larger number of significant figures.

Conventions for Reporting and Interpreting Reported Values

1. Numerical values are typically considered uncertain in the last digit by ±3 or more, with perhaps slight uncertainty in the next-to-last digit by up to ±2.
2. If the last digit to be retained is a one or two, an additional digit is retained so that precision is not inappropriately reported due to rounding.

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3.4: Least Squares Linear Regression

Your experimental data will usually be examined in graphic form, which can be more instructive than tabulated data. In any graphic presentation, be sure to plot your independent variable on the abscissa (x-axis) and the dependent variable on the ordinate (y-axis).

If the data are presented in graphic form, the usual procedure is to fit the best curve through the experimental points. As Brownlee[3] puts it,

> "When an investigator observes simultaneously two variables, x and y, usually with good reason he plots the observations on a graph. If there is any sign of an association, he is usually seized with the impulse to fit a line, usually a straight line or, rather infrequently, a parabola or cubic."

When we are "seized with the impulse" to fit a straight line curve the process of curve fitting is called linear regression. We assume that the deviations of the dependent variable y are distributed normally (that is, a Gaussian distribution). This assumption is not required for the determination of the least squares parameters, but it is necessary for construction of confidence intervals or for tests of hypotheses about the parameters. The parameters obtained by least squares under these conditions are unbiased and provide the best estimates of the curve fitting parameters.

Most of the experimental data that you will encounter this semester will have a simple functional form, or can be manipulated in such a way as to assume a simple form. We shall assume here that our data follows a linear relationship. For example, consider a gas that is thought to follow the equation of state

$$\begin{gathered} \mathrm{Z} \equiv \frac{\mathrm{PV}}{\mathrm{nRT}} = \mathrm{B}_0 + \mathrm{B}_1\mathrm{P} \\ \mathrm{y} = \mathrm{a} + \mathrm{bx} \end{gathered} \tag{3.4.1}$$

Measurements of Z, called the compressibility factor, are made at each of a series of pressures in an effort to determine B_0 andB_0. The least squares approach can be used to determine the slope (b, orB_1) and y-intercept (a, or B_0) which define the best straight line that can be drawn through the data. In simple linear regression analysis, it is assumed that all the error in the measurement lies in the dependent variable (y). This is equivalent to assuming that the precision of the determination of the independent variable (x) is considerable higher than that of y. The measured value of some quantity (y_i) will differ from the value predicted by a linear equation ($y = a + bx$) by an amount r_i called the residual.

$$r_i = y_i - a - bx \tag{3.4.2}$$

The least squares approach identifies the best straight line as the one for which R, the sum of the squares of the residuals, has the smallest value:

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} (y_i - a - bx_i)^2 \tag{3.4.3}$$

The arrows in Figure 4 represent the residuals, and all of them are equally weighted.

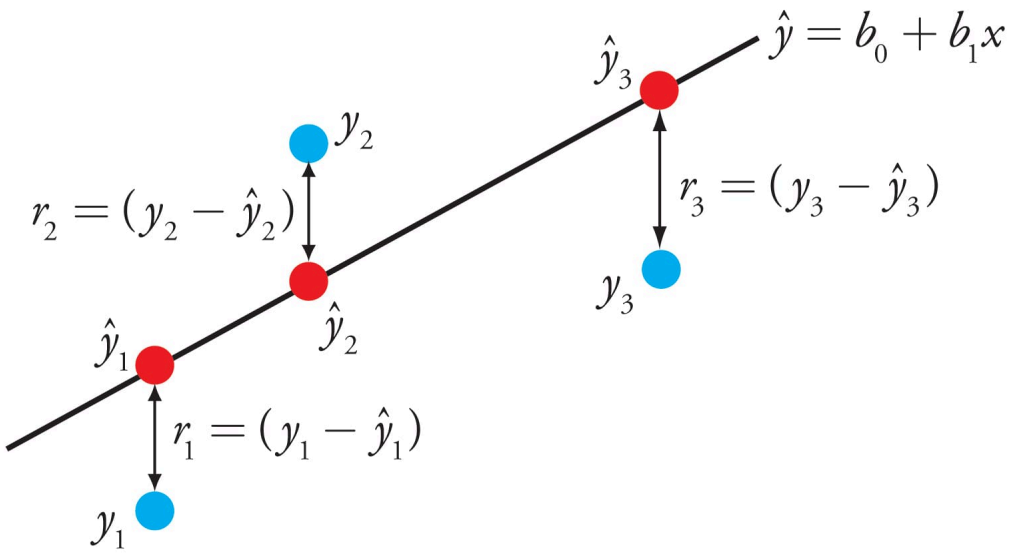


Figure 3.4.1: Least Squares Linear Regression: *Illustration showing the evaluation of a linear regression in which we assume that all uncertainty is the result of indeterminate errors affecting y. The points in blue, y_i, are the original data and the points in red, $\hat{y}_i$, are the predicted values from the regression equation, $\hat{y} = b_0 + b_1 x$. The smaller the total residual error, the better the fit of the straight-line to the data* (source)

We want to minimize the sum of the squares of the residuals. That is, we want to make *least* the sum of *squares* of residuals, and, thus, the name of the procedure. Since this is a minimization problem, we require that R be as small as possible with respect to a and b by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial a}\right)_b = -2\sum(y_i - a - bx_i) = 0 \tag{3.4.4}$$
$$\left(\frac{\partial R}{\partial b}\right)_a = -2\sum((y_i - a - bx_i)(x_i)) = 0$$

Solving equations 3.4.4 simultaneously, we obtain

$$a = \frac{(\sum x_i^2)(\sum y_i) - (\sum x_i)(\sum x_i y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{3.4.5}$$

$$b = \frac{N(\sum x_i y_i) - (\sum x_i)(\sum y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{3.4.6}$$

While we ultimately want to fit the data to $y_i = a + bx_i$ for a series i of N points, the theoretical development is much easier if we use $y_i = c + b(x_i - \overline{x})$ where obviously a and c are related by $a = c - b\overline{x}$, and where $\overline{x}$ is simply the mean of the x data, $n\overline{x} = \sum_{i=1}^{N} x_i$. This designation of variables is better because "it turns out" that in this approach the parameters b and c are independent, their variances are independent, and the formulas to transform to the parameters a and b are simple. Again, we want to minimize the sum of the squares of the residuals $r_i = y_i - c - b(x_i - \overline{x})$, R.

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} [y_i - (c + b(x_i - \overline{x}))]^2 \tag{3.4.7}$$

Now we require that R be as small as possible with respect to b and c by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial c}\right)_b = -2\sum(y_i - c - b(x_i - \overline{x})) = 0 \tag{3.4.8}$$
$$\left(\frac{\partial R}{\partial b}\right)_c = -2\sum((y_i - c - b(x_i - \overline{x}))(x_i - \overline{x})) = 0$$

These two equations are readily rewritten as

$$\begin{aligned} \sum y_i &= \sum c + \sum b\left(x_i - \overline{x}\right) \\ \sum y_i\left(x_i - \overline{x}\right) &= \sum c\left(x_i - \overline{x}\right) + \sum b\left(x_i - \overline{x}\right)^2 \end{aligned} \tag{3.4.9}$$

which, since $\sum\left(x_i - \overline{x}\right) = 0$, simplify to

$$\begin{aligned} c &= \frac{\sum y_i}{N} = -\overline{y} \\ b &= \frac{\sum y_i\left(x_i - \overline{x}\right)}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{3.4.10}$$

The knowledge of c and b then allows us to determine the parameter, a, $a = c - b\overline{x} = \overline{y} - b\overline{x}$, a particularly simple relation.

The variance and standard deviation of N data points was introduced previously. The appropriate treatment of the parameters c and b in the least squares procedure results in

$$\begin{aligned} V[c] &= \frac{s^2}{N} \\ V[b] &= \frac{s^2}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{3.4.11}$$

where

$$s^2 = \frac{1}{N-2}\sum\left(y_i - c - b\left(x_i - \overline{x}\right)\right)^2 = \frac{1}{N-2}\sum\left(y_i - a - bx_i\right)^2 = \frac{R_{min}}{N-2} \tag{3.4.12}$$

Because c and b are independent quantities, it can be shown that

$$\begin{aligned} V[a] &= V[c] + \overline{x}^2 V[b] \\ &= \frac{s^2}{N} + \overline{x}^2\frac{s^2}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{3.4.13}$$

The standard deviations of a and b, σ_a and σ_b, are then obtained by taking the square roots of V[a] and V[b].

Another statistic that is sometimes used is the *correlation coefficient,* r. It is given by the expression

$$r = \frac{N\sum x_i y_i - \sum x_i \sum y_i}{\sqrt{\left(N\sum x_i^2 - \left(\sum x_i\right)^2\right)\left(N\sum y_i^2 - \left(\sum y_i\right)^2\right)}} \tag{3.4.14}$$

When the absolute value of r is close to unity the correlation between the y and x data is good, when it is close to zero the correlation is poor. Because the correlation coefficient is sometimes hard to interpret, it is usually better to work with the standard deviations of the regression parameters, σ_a and σ_b.

Linear regression is a powerful tool that takes the guesswork out of obtaining best fit information. However, like all mathematical tools, it must be used with caution. While the standard deviations and the correlation coefficient give indications of the goodness of the fit, there is no substitute for graphing the data and looking at the result. Since the errors are assumed to be random, the y_i values should be scattered about the best fit straight line in a random fashion. The residuals should likewise be either positive or negative (and sum to zero) without any pattern. If the data show a pattern of curvature, it is possible that the results do not conform to the linear model proposed. A linear regression is *not* valid in this case. You should also be alert to the effects of systematic errors, which may change the slope or the intercept without affecting the linearity of the data.

Linear regression of the type discussed above relies on a number of critical assumptions. Among the most important is that all the uncertainty in each of the y values is the same. If the form of the equation required to provide a linear relationship produces an independent variable that contains a significant uncertainty, the set of conditions that produced the minimum in the residuals of the line may not be the set that actually minimizes the uncertainty in the data. In this case, a "non-linear" least squared technique such as simplex is recommended.

Note

In this course, you can use the MatLab lsq.m script to perform least squares analysis. The equations given above are included in the lsq script.

Weighted Least Squares Analysis

When measurements of the dependent variable incur different uncertainties, a ***weighted*** least squares technique should be used. In this approach, each residual ri is divided by a factor proportional to its uncertainty ε_{y_i}. Then R, the sum of the squares of the residuals, becomes

$$R = \sum_{i=1}^{N} \frac{r_i^2}{\varepsilon_{y_i^2}} = \sum_{i=1}^{N} \frac{1}{\varepsilon_{y_i^2}} (y_i - a - bx_i)^2 \tag{3.4.15}$$

Using the same minimization techniques described above, the slope and intercept for weighted least squares become

$$a = \frac{\sum \frac{x_i^2}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2} \right)^2} \tag{3.4.16}$$

$$b = \frac{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2} \right)^2} \tag{3.4.17}$$

Weighted least squares has utility in a number of applications in the physical chemistry laboratory. One common situation arises when a linear equation requires the log of a measured quantity to be the dependent variable. Consider for example, the measurement of vapor pressure. Most pressure sensing devices will provide a constant error in the measurement of P. If the dependent variable to be plotted is lnP, however, its uncertainty is not constant but decreases as P increases. Thus,

$$\varepsilon_{lnP} = \frac{\partial lnP}{\partial P} \varepsilon_P = \frac{\varepsilon_P}{P} \tag{3.4.18}$$

An appropriate weighting factor in this case would be $\varepsilon_{y_i} = \frac{1}{P}$.

When you use Matlab for data analysis this semester, the command **lsq(x,y)** will be used for least squares analysis of x, y data, and the command **wtlsq(x,y)** will be used for weighted least squares analysis. In the latter case, you will be asked for a weighting factor, e. In either case, the program will output the least squares slope, y-intercept, correlation coefficient, standard deviation of the slope, and standard deviation of the intercept.

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3.5: Rejection of Outliers (Q-test)

In a set of collected data, there may be one or more values that deviate markedly from the trend of the others; in other words, there may be one or more data points that seem suspicious. If a measurement appears suspicious, we need evidence before deciding that it is statistically discordant with the rest of the data. One tool for doing this is the **Q-test**.

> **You should not reject a piece of data that seems suspect until you perform a Q-test**.

In a set of data of three to ten measurements, the Q-test can be performed on a single suspicious data point as follows:

$$Q_{exp} \equiv \frac{|\text{ (suspected outlier's value) } - \text{ (value closest to it) }|}{\text{(highest value) } - \text{ (lowest value)}} \tag{3.5.1}$$

The following table provides critical values for $Q_{critical}(\alpha, n)$, where:

- α is the probability of incorrectly rejecting the suspected outlier,
- n is the number of samples in the data set.

Table 3.5.1: Critical Values for Dixon's Q-Test

$\frac{\alpha \longrightarrow}{\text{no. of samples}\downarrow}$	$Q_{critical}$ $\alpha = 0.1$ **(90% confidence limit)**	$Q_{critical}$ $\alpha = 0.05$ **(95% confidence limit)**	$Q_{critical}$ $\alpha = 0.04$ **(96% confidence limit)**	$Q_{critical}$ $\alpha = 0.02$ **(98% confidence limit)**	$Q_{critical}$ $\alpha = 0.01$ **(99% confidence limit)**
n = 3	0.941	0.970	0.976	0.988	0.994
n = 4	0.765	0.829	0.846	0.889	0.926
n = 5	0.642	0.710	0.729	0.780	0.821
n = 6	0.560	0.625	0.644	0.698	0.740
n = 7	0.507	0.568	0.586	0.637	0.680
n = 8	0.468	0.526	0.543	0.590	0.634
n = 9	0.437	0.493	0.510	0.555	0.598
n = 10	0.412	0.466	0.483	0.527	0.568

The Q-test:

Compare the value of Q_{exp} from the equation above to the critical value of $Q_{critical}$.

- If $Q_{exp} \geq Q_{critical}$ then the suspect value can be rejected.
- If $Q_{exp} \leq Q_{critical}$,the value should be retained in the data set.

For additional information consult Rorabacher, D. B. "Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's 'Q' Parameter and Related Subrange Ratios at the 95% confidence Level," *Anal. Chem.* **1991**, *63*, 139–146. (see also http://chem-net.blogspot.com/2013/01...atistical.html)

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3.6: Guidelines for Managing and Reporting Uncertainty in Experiments

Always consider uncertainty during an experiment, record it in your ELN, and include it in all calculations and reporting. Do not leave the lab until you are sure that you have a valid strategy for determining errors in all final values.

1. **Uncertainty Awareness:**
   Before leaving the lab area, ensure you have a valid strategy for estimating uncertainties in all measured and calculated values.

2. **Estimating Uncertainty During Measurements:**

   - **Equipment Uncertainty**: Record uncertainties provided by equipment or manufacturers (e.g., balance deviation, pipette error). If unavailable, assume uncertainty is ±0.5 of the smallest measurable unit.
   - **Replicates**: For three or more measurements, calculate the standard deviation of the mean.
   - **Function-Based Values**: Perform propagation of error analysis.
   - **Least Squares Fitting**: Use errors from fitted parameters (e.g., slope or intercept) and propagate uncertainty if used in further calculations. Avoid linear regression if data deviates significantly from linearity.
   - **Consult Instructors**: Seek help for unclear sources of uncertainty.

3. **Propagation of Error:**
   Combine individual uncertainties to estimate the overall uncertainty of the final result. Use partial derivatives where necessary, and assume constants (e.g., RR) are error-free.

4. **Reporting Results:**

   - Include propagated uncertainty with each result.
   - Compare results with literature values using percent or absolute error.
   - Ensure significant figures reflect uncertainty and justify their use.

5. **Replicate Measurements:**

   - Report the mean and precision (e.g., standard deviation).
   - Use the Q-test to justify excluding outliers.

6. **Single Measurements:**

   - Estimate and report uncertainty (random or systematic).
   - Compare accuracy to expected values if available.

7. **Least Squares Fitting:**

   - Use weighted or non-weighted regression based on data.
   - Reject outliers only using the Q-test on residuals.
   - Propagate uncertainty from fitted parameters to calculated values.

8. **Qualitative Uncertainty:**

For variables with no clear quantitative uncertainty, discuss potential sources and their impact on results. Provide reasonable estimates and substantiate with evidence.

9. **Before Leaving the Lab:**
    - Confirm all uncertainties are documented.
    - Check for systematic errors (e.g., calibration issues).
    - Ensure thorough records of measured values and associated uncertainties.

By following these steps, you ensure your experimental results are accurate, reproducible, and clearly reported.

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3.7: Homework Problems

📅 **Pre-lab Due**: Attempt all seven problems before 1 pm on the scheduled meeting on this topic (see syllabus agenda). Your pre-lab assignment will be graded based on evidence of sincere effort, and work shown, but not on accuracy.

📅 **Final Problem Set Due**: The final problem set is due at 1 pm one week after our scheduled meeting on this topic (see syllabus agenda). The final problem set will graded based on work shown, thorough and accurate responses to questions, accuracy of calculation, and correct reporting (including units).

🎯 **Purpose:** Learn how to correctly estimate experimental uncertainty, and how to correctly report a value and its estimated uncertainty. This practice will get you ready to perform uncertainty analysis for your own experimental measurements this semester (and in the future).

Each practice problem below requires that you correctly apply either **statistical analysis** or **propagation of uncertainty** to estimate the uncertainty in a calculated value. Each problem also asks you to correctly report calculated values and their uncertainties.

Uncertainty analysis

This is the expected workflow for analysis of experimental values in P-Chem Lab:

Calculate → estimate uncertainty → report value ± uncertainty appropriately → justify the reporting → interpret what the uncertainty tells you.

Python (using Jupyter Notebooks in CoLab) is the recommended tool for completing this problem set. However, you may complete this assignment using any tool including pencil and paper, excel, etc. **You must understand the work you do, thus you may not use AI to complete this assignment.**

After submitting your initial attempts before the meeting, you will work with other students during our meeting to reach consensus about the strategies used to answer each question, and how to report each value and its uncertainty. Your instructors will be with you to answer your questions and to help guide your discussions. After the meeting, you will submit your revised work and final answers.

Your answers to these problems may be hand-written or typed. However, any submissions that are deemed illegible, unclear, or poorly organized will not be accepted.

Note

(1) We recommend that you use python to complete this problem set – we have provided some CoLab notebooks to help guide you. However, you may use whatever technology (calculators, software, etc.) you like to aid in working these problems.

(2) No matter what tools you use, it is important to show how your calculations are set-up and, where appropriate, give a sample calculation. Simply giving the final answer is not acceptable.

(3) In reporting all results, you should always round your reported answer to be consistent with your estimated uncertainty. For example: a calculated result of 56.2189 ± 0.0386 would be reported as **56.20 ± 0.04** where 0.04 is the standard deviation or propagated uncertainty. *See reading assignments for details about reporting*.

The seven problems are below. Note that there are custom CoLab tutorials to help you through this problem set. See Canvas and/or your Google Classroom to find the tutorials.

PROBLEM 1: Estimate Uncertainty using Statistics

A student makes five independent measurements of each of the linear dimensions of a box. The results are tabulated as follows:

Measurement	Length (cm)	Width (cm)	Height (cm)
1	1.010	5.376	2.001
2	1.015	5.339	2.105
3	1.013	5.385	1.985
4	0.999	5.375	1.989
5	1.009	5.369	2.008

A. **Summarize the measurements:** calculate the mean ($\bar{x}$), sample standard deviation (s), and relative standard deviation ($\%RSD = \frac{s}{\bar{x}} \times 100$). Report $\bar{x} \pm s$, and $\%RSD$ for each dimension (length, width, height) using appropriate units and appropriate precision.

B. **Compare the precision of the measurements**: Which dimension was most precise? ...least precise? Explain what statistical parameters from calculations in (A) are the most appropriate for comparing the precision of measurements that have different magnitudes. Support your answers using calculated values from (A).

C. **Calculate the volume**: Each row of the table represents one set of independent measurements of the box.
   - Calculate volume for each trial. This should produce five calculated volumes from the independent measurements of length, width, and height.
   - Then calculate the mean ($\bar{x}$), sample standard deviation (s), and relative standard deviation ($\%RSD$).
   - Report $\bar{x} \pm s$, and $\%RSD$ for volume using appropriate units and appropriate precision.

D. **Interpret results and justify choices for reporting:** Write a short paragraph that addresses the following points.
   - Which measurement (length, width, height) contributes the greatest uncertainty to the calculated volume?
   - Does the calculated volume appear to be more or less precise that the individual measurements? Explain, using evidence from your calcuations to support your argument.
   - Justify your choices in reporting to appropriate precision; in other words, what justifies "appropriate precision" of these values.

PROBLEM 2: A Simple Case for Propogation of Uncertainty

A student weighs a sample using an analytical balance, with an estimated uncertainty of ±0.5 mg in each measurement. Using the data below, determine the mass of the sample and the propagated uncertainty in that mass.

Item measured	Mass (g)
Sample and flask	5.1647 ± 0.0005
Empty flask (tare)	2.3712 ± 0.0005

A. Calculate the mass of the sample.
B. Calculate the propagated uncertainty in the sample mass.
C. Report the sample mass $\pm$ uncertainty: report using appropriate units and precision.
D. Explain why the propagated uncertainty is larger than the uncertainty in either individual mass measurement.
E. Justify the number of decimal places used in your final reported answer.

PROBLEM 3: Statistics and Rejection of Discordant Data

An investigator measures photon emission from the reaction shown below. The emitted photons (at 589 nm) are detected using a photomultiplier. For each run, the investigator measures both the total counts (signal + background) and the background counts.

$$Na^+ + O^- \rightarrow Na^* + O \overset{h\nu}{\rightarrow} Na + O$$

Run #	**Signal + Background (counts/sec)**	**Background (counts/sec)**
1	1500	1000
2	1200	1250
3	1375	1100
4	1425	900
5	1280	1200
6	1490	1363

The signal of interest is obtained by subtracting the background from the signal + background measurement.

A. **Determine the signal for each run.** Examine the resulting values before doing any further calculations. What do you notice about the data?
B. **Calculate the mean and standard deviation of the signal measurements.** Your software will probably display more digits than are meaningful. **Do not simply copy the numbers produced by the computer.** Decide how the mean and standard deviation should be reported, and explain your reasoning.
C. **One or more of these measurements might look suspicious.** Should any measurement be removed simply because it looks unusual? Explain briefly.
D. **Use the Q-test at the 90% confidence level to determine whether there is statistical justification for rejecting the suspicious measurement(s) as discordant.** Clearly identify the value(s) you test and compare Q_{calc} with Q_{crit}.
E. **Based on your statistical analysis, report your best estimate of the signal and its uncertainty.** Explain what the standard deviation tells you about the precision of this measurement, and is the standard deviation sufficient for estimating uncertainty? What other ideas might guide your decision for how to report the final value?

PROBLEM 4: Least Squares Analysis and Rejection of Discordant Data

The following experimental data are expected to show an approximately linear relationship between x and y.

Data Point	1	2	3	4	5	6	7
x	26	30	44	50	62	68	74
y	92	85	78	81	54	51	40

Your goal is to determine whether a linear model reasonably describes these data and to investigate whether there is statistical justification for rejecting any observation as an outlier.

A. **Plot and examine the data:** Create a scatterplot of y versus x. Before performing a regression, describe what you see.
   - Does a linear relationship appear reasonable?
   - Is the relationship positive or negative?
   - Does any point look unusual? If so, identify it.

B. **Fit a linear model:** Perform a linear least-squares regression and determine the slope, intercept, and correlation coefficient, r.
   - Add the best-fit line to your plot.
   - Report the equation of the fitted line on the plot, using an appropriate number of digits.
   - Report both the value and uncertainty for the slope and intercept. Justify your choices in reporting to appropriate precision; in other words, what justifies "appropriate precision" of these values.
   - Then interpret your result:
     - What does the **sign** of the correlation coefficient (r) tell you?
     - What does the **magnitude** of r tell you?
     - Does a large value of $|r|$, by itself, demonstrate that every observation is well described by the model? Explain.

C. **Examine the residuals:** For each observation, calculate the y-residual from the equation below (3.7.1) and create a plot of residual versus x.

$$\text{residual} = y_i - y_{predicted,i} \tag{3.7.1}$$

   - If the linear model adequately describes the data, what would you expect the residuals to look like?
   - Examine your residual plot. Do you see evidence of a systematic pattern, or does one observation appear particularly unusual? Identify the observation you would investigate further and explain your choice.

D. **Test the suspicious data point:** A point that looks unusual should not be discarded simply because removing it might improve the fit. Apply the **Q-test to the y-residuals** to determine whether there is statistical justification for rejecting the questionable observation. Compare Q_{expt} with the appropriate Q_{crit} at the **90% confidence level**. Based on this comparison, is there statistical justification for rejecting the observation? Explain your decision.

E. **What happens if the point is removed?** Regardless of your decision in Part D, temporarily remove the questionable observation and repeat the linear regression (Parts A, B, C above). This is an exploration, not permission to discard the measurement. Compare the regression **with and without** the suspicious data point. Consider slope, intercept, correlation coefficient r, and residuals.

F. **Make a scientific argument.** Did removing the questionable point substantially change the relationship between x and y? Support your conclusion with quantitative evidence from the two regression analyses.

PROBLEM 5: Propagation of Uncertainty

In a chemistry lab, students obtain the following data and are asked to find the **molecular weight (MW) of methanol** using the

ideal gas law, $PV = nRT$.

	Pressure (methanol)	Temperature	Mass (of methanol)	Volume
Trial 1	72.5 ± 0.5 mm Hg	295.10 ± 0.05 K	0.1331 ± 0.0002 g	1.05678 ± 0.00005 L
Trial 2	72.0 ± 0.5 mm Hg	295.05 ± 0.05 K	0.1329 ± 0.0002 g	1.05678 ± 0.00005 L

A. **Develop the function and determine MW**. Use the ideal gas law and the measured quantities to write a single expression for the molecular weight of methanol in grams per mole. Then calculate the molecular weight independently for each trial. ***Reminder**: pay attention to units, and perform unit conversions as necessary.*
B. **Propagate the uncertainty**. Determine the uncertainty in the molecular weight calculated for each trial. Clearly identify the uncertainty associated with each measured quantity and show how those uncertainties enter your calculation.
C. **Analyze the sources of uncertainty.** Which measured quantity contributes most strongly to the uncertainty in the calculated molecular weight? Support your answer quantitatively.
D. **Determine the average molecular weight and its uncertainty.** Calculate the average molecular weight determined from the two independent trials. Treat the two molecular wights as independently measured quantities and propagate their uncertainties through the calculation of the average. Report the average molecular weight and its uncertainty using appropriate units and precision.
E. **Justify your choices in reporting**. Explain how you determined the appropriate precision for the reported average molecular weight and its uncertainty.

PROBLEM 6: Propagation of Uncertainty

The Arrhenius relationship allows us to determine the activation energy for a reaction by measuring the rate constant at two different temperatures, according to the following expression.

$$ln\left(\frac{k_2}{k_1}\right) = -\frac{E_{act}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3.7.2}$$

The rate constants for the reaction below was measured at two temperatures.

$$2DI \rightarrow D_2 + I_2$$

$k_{660} = (1.2 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $660 \pm 2K$

$k_{720} = (1.8 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $720 \pm 2K$

A. **Develop the function and determine the activation energy**. Use the Arrhenius expression (eq. 3.7.2) to develop a function for calculation of E_{act}. Then use the two independent measurements of k and T to calculate the E_{act}.
B. **Propagate the uncertainty in E_{act}.** Develop the function for calculation of uncertainty and determine the uncertainty in the value of E_{act}.
C. **Report and interpret the results.** Report E_{act} and its uncertainty using appropriate units and precision. Justify your choices in reporting.
D. **Analyze the sources of uncertainty.** Compare the contributions from k_1, k_2, T_1, and T_2. Which measurement(s) have the greatest influence on the uncertainty in E_{act}? Support your answer quantitatively.

PROBLEM 7: Propagation of Uncertainty

In the method of Clement and Desormes, the heat capacity (C) ratio of an ideal gas is determined from the manometrically determined values of P_1, the gas pressure at temperature T_1; P_2, the gas pressure immediately after a reversible adiabatic expansion when the temperature is T_2; and, P_3, the gas pressure after the gas has warmed back up to temperature T_1. The relationship used to calculate the heat capacity ratio is given by equation 3.7.3.

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{C_V}{R} + 1}{\frac{C_V}{R}} \tag{3.7.3}$$

where

$$\frac{C_V}{R} = \frac{P_2\left[1 - \left(\frac{P_3}{P_1}\right)\right]}{P_3 - P_2} \tag{3.7.4}$$

The following pressure data were collected:
P_1 = 763.1 ± 0.2 mmHg
P_2 = 757.0 ± 0.1 mmHg
P_3 = 758.7 ± 0.2 mmHg

A. **Develop the function and determine the heat capacity ratio, γ.** Use the equations above (eqs. 3.7.3 and \{refCD2}) to develop a function to calculate γ from the three pressure readings given above. Then use the function to calculate the value of γ.
B. **Propagate the uncertainty in each measured pressure to determine uncertainty in γ.** Calculate the uncertainty in the heat capacity ratio, γ.
C. **Report and interpret the result.** Report γ and its uncertainty with appropriate precision and units, if applicable. Justify your choices in reporting. Based on your uncertainty analysis, what can you conclude about the precision with which this experiment determines γ?

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3.8: References and Additional Reading

1. Shoemaker, D.P.; Garland, C.W.; Nibler, J.W. Experiments in Physical Chemistry, 6th Edition, McGraw-Hill, New York, NY, 1996, pp 27-89.

2. Bettelheim, F. A., Experimental Physical Chemistry, W.B. Saunders Co., Philadelphia, 1971, Chapter 2.

3. Brownlee, K. A., Statistical Theory and Methodology in Science and Engineering, 2nd Edition, John Wiley and Sons, Inc., New York, New York, 1965, pp 334-338.

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4: ABSORPTION SPECTRUM OF CONJUGATED DYES

You will measure the absorption spectra of a series of conjugated dyes and then use the Particle-In-A-Box (theoretical model) to explain the observed spectra.

The general approach to this experiment is adapted from D. P. Shoemaker, C. W. Garland, and J. W. Nibler, Experiments in Physical Chemistry, 6th edition, McGraw Hill Co. Inc, NY, 1996, p378. The experiment has been revised to suit our laboratory environment.

4.1: Pre-lab Assignment

4.2: Proceedure (Part I) – Collect Spectra, Apply PIB

4.2.1: Instructions for using the UV-Vis Spectrophotometers

4.2.2: Introduction to Particle in the Box (PIB) applied to Dyes

4.3: Proceedure (Part II) – Hückel Calculations Using Hulis (Part II)

4.3.1: Introduction to Hückel Theory

4.4: References and Additional Reading

References:

1. Castellan, G. W., Physical Chemistry, Addison-Wesley, Reading, Mass., 1972, Chapters 19-22.

2. Barrow, G. Physical Chemistry, 3rd ed., McGraw-Hill, New York, NY, 1973, Chapters 3 and 12.

3. Shoemaker, D. P., Garland, C. W., and Nibler, J. W. Experiments in Physical Chemistry, 6th ed., McGraw-Hill, NY, 1996, Chapter XIV, Experiment 34.

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6. Kuhn, H., J. Chem. Phys., **1949**, 17, 1198.

7. Herzfeld, K.F.; Sklar, A. L. Rev. Mod. Phys., **1942**, 14, 294.

8. Silbey, R. J., Alberty, R.A., and Bawendi, M.G., Physical Chemistry, 4th ed., Wiley, NY, 2005, Chapter 9, Section 9.6; Chapter 11, Section 11.7.

9. Cotton, F.A., "Chemical Applications of Group Theory", Wiley, New York, 1971, Section 7.1 and pp. 366-367.

10. Suzuki, H., "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, 1967, Chapter 17, p. 374.

11. Aldrich Catalog, Aldrich Chemical Company, Inc., 1992., found in FFSC 1113 or online.

12. Venkataraman, K., "The Chemistry of Synthetic Dyes", Academic Press, Inc., NY, 1952, Volume II, Chapter XXXVIII, p. 1155.

13. Streitwieser, A., "Molecular Orbital Theory for Organic Chemists", John Wiley & Sons, Inc., NY, 1967, Chapter 2.

14. Okawara, M., Kitao, T., Hirashima, T., and Matsuoka, M., Physical Sciences Data 35: Organic Colorants, Kodansha, Tokyo; Elsevier, Amsterdam-Oxford- New York-Tokyo, 1988, pp. 318-321.

15. Taubmann, G., J. Chem. Ed., **1992**, 69, 96.

16. Atkins, P.W. Physical Chemistry, 5th ed., W. H. Freeman, NY, 1994, Sections 12.1, 14.9, or, 6th ed., W. H. Freeman, NY, 1997, Sections 12.1, 14.9.

17. Engel, T., Drobney, G and Reid, P., Physical Chemistry for the Life Sciences, Pearson Prentice Hall, NJ, 2008 (Section 14.3).

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4.1: Pre-lab Assignment

📅 **Due:** This assignment must be completed before 1:00 PM on your scheduled lab meeting day (see syllabus schedule).

🕒 **Time:** Plan at least two hours to complete this assignment.

🎯 **Purpose**: This pre-meeting assignment is designed to help you arrive to the meeting prepared to engage in thoughtful discussion and to conduct the experimental work.

This module includes **Wet Lab** work, thus you should prepare for your meeting by dressing appropriately for lab and bringing your own safety eyewear. In addition, for this and all following meetings, there is a written pre-lab assignment as described below. Because all experimental modules require similar preparation, the pre-lab assignment is divided into a "General" assignment that should be completed for each module and a "Specific" assignment for each meeting.

GENERAL Pre-Lab Assignment

A template file for preparing your pre-lab assignment is available in your Google Classroom Assignments.

Read the module in canvas and in the lab manual, follow the instructions within, then write a brief **introduction** to the experiment and an **experimental plan** using the following outline:

I. **Description of the Experiment:** In your own words, briefly introduce the topic, describe the theory upon which the experiment is based, and state the goals for this experiment. Keep it concise; lengthy discussions or derivations of equations are unnecessary.
   a. Background (importance/relevance): A brief description and justification of the importance of the topic, *with at least two references to source material* (do not use the lab manual as a reference). Describe the topic, and describe why is it interesting, important, and worth your time to learn.
   b. Theory: A concise paragraph or more describing the general theory for the method/technique used; this section should contain a reference to the appropriate pages of the textbook, or other source material from the literature.
   c. Goals/Purpose: Brief statement of purpose, which should indicate what is analyzed and the technique used. Limit to three to five sentences.

II. **Experimental Plan:** a short summary of the specific things that you would need to know in order to do the experiment without having access to your lab manual, with the understanding that you will always have a TA available to teach you how to use the instrument.

    The best way to approach this task is to thoroughly read the procedure for the experiment. While reading, take notes on the specifics of the work. What chemicals will you use? If you have to make solutions, what solutions do you need to make and of what concentration? How will you prepare them? What instrument will you use, and what specific instrument settings will you need to input (sometimes you will find this information in the Appendices that discuss the use of the instruments)? How many runs of each sample will you do; and over what wavelength, or temperature, etc. range? You do not need to write down how to use the instrument; we will teach you that. Bottom Line: we want you to write down only that pertinent information about samples, sample preparation, instrument and instrument parameters, numbers of runs, and other things, that you will need to know in order to do your work.

In addition to the general pre-lab assignment, please complete the specific tasks listed below. Your assignment must be submitted on Canvas before the deadline.

SPECIFIC Pre-Lab assignment for Absorption Spectra of Conjugated Dyes

1. Complete the general pre-lab assignment.

2. **Find structures for the four dyes to be studied in this experiment.** This information is readily available on the Sigma-Aldrich web site (http://www.sigmaaldrich.com) by searching for the name of each dye. Use ChemDraw to create a figure that shows the full chemical name, abbreviated name (Dye 1, etc), and the skeletal structure of each dye. It is unnecessary to include the counterion (iodide or chloride) in your stuructures. Include this figure in your pre-lab assignment.
   - **Dye #1**: 1,1'-diethyl-2,2'-cyanine iodide
   - **Dye #2**: 1,1'-diethyl-2,2'-carbocyanine chloride
   - **Dye #3**: 1,1'-diethyl-2,2'-dicarbocyanine iodide
   - **Dye #4**: 1,1'-diethyl-4-4'-carbocyanine iodide
3. **Use your knowledge of HOMO and LUMO to answer the questions below.**
   a. Give a definition of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).
   b. How are HOMO and LUMO related to UV-Vis absorption spectroscopy, specifically in the context of the λ_{max} values of these dyes?
   c. How does the HOMO-LUMO energy gap change as the length of a conjugated π system increases? (consider your knowledge from organic chemistry)
4. Examine the **structure** of each dye (specifically the length of the conjugated chain between the N atoms).
   - Compare and contrast the structures of the four dyes.
   - Based on the **particle in a box model** ($\Delta E = \frac{(N+1)h^2}{8mL^2}$) , where L is the length of the box, what trend do you expect in the λ_{max} values of this series of dyes? Justify your prediction.
5. Using your knowledge of **Beer's Law**, draw absorbance spectra in the range of 400 - 800 nm (example blank plot axes provided below).
   a. On plot A and B, sketch the spectrum of a dye molecule that absorbs light with $\lambda_{max} = 700$ nm at absorbance of 0.8 A.U.
   b. On plot A, add the spectrum of the same dye at half of the original concentration.
   c. On plot B, add the spectrum of a second dye that has $\lambda_{max} = 500nm$.
   d. On plot B, in a separate color or line thickness, show the spectrum that would occur if the two original dye solutions were mixed together in equal portions.
   e. Provide a concise justification of your predicted spectra; specifically justify your prediction for how the spectrum changes upon dilution (plot A) and how the spectrum changes upon mixing (plot B).

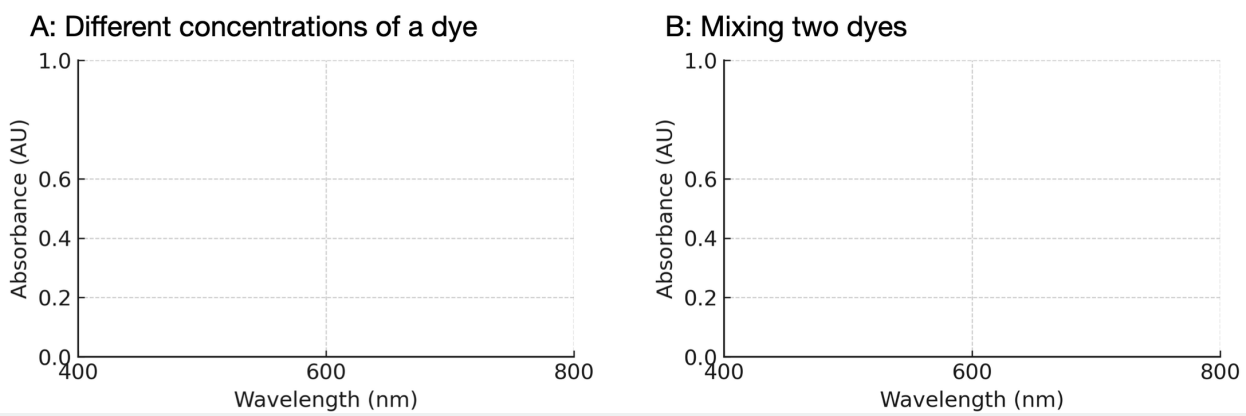


Figure 4.1.1: Predicted Absorption Spectra of Dyes. A) Shows a Dye with $\lambda_{max} = 700$ at two different concentrations. B) Shows predicted spectra of two dyes before and after mixing. (CC-BY-NC-SA; Kathryn Haas 2025)

6. Read one of the following (Duke students click here):
   - Change, R., Physical Chemistry for the Chemical Sciences, University Science Books, CA, 2014 (Section 10.9)
   - Chang, R., Physical Chemistry for the Chemical and Biological Sciences, University Science Books, CA, 2000 (Section 14.8)

Additional reminders

Since this is the first time you will be going into lab, we recommend reviewing the Chemistry Department Safety Manual and the Orientation Module. Here are some critical reminders:

- **Wear Protective Clothing**: As always, please dress appropriately for a laboratory environment. You will not be permitted to

enter lab, and thus will lose the opportunity to participate in the course assignments, if you fail to dress appropriately.

- **Prepare by completing the Pre-Lab Assignment**: It is absolutely essential that each student be prepared for lab meetings by reading the appropriate module in this manual, and by completing the specified pre-laboratory assignments. The pre-lab assignment must be submitted as a single pdf document on Canvas before the scheduled lab meeting. The pre-laboratory assignments are designed to prepare you to operate efficiently and safely during the experimental module. You will not be allowed to conduct experiments if the pre-lab assignment is not completed before your lab meeting. If there is an extenuating circumstance that prevents your preparation, please inform your instructors as soon as possible.
- Your preparedness will be evaluated by the quality of your work on pre-lab assignments, your answers to oral questions pertaining to the laboratory from the instructors, and/or your responses to unannounced quizzes and skills checks.

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4.2: PROCEEDURE (PART I) – COLLECT SPECTRA, APPLY PIB

Materials

- **Equipment:**
  - UV/Vis spectrometer (you will use either an Agilent Cary 60 Spectrometer or an Agilent Cary 100 Spectrometer)
  - Cuvettes (you will use glass cuvettes, which are optically transparent to visible (but not to UV) light)
- **Reagents:**
  - Reagent grade methyl alcohol (methanol)
  - Stock solutions of four polymethine dyes dissolved in methanol (solutions are approximately 10^{-4} M):
    - 1,1'-diethyl-2,2'-cyanine iodide
    - 1,1'-diethyl-2,2'-carbocyanine chloride (also known as pinacyanol chloride)
    - 1,1'-diethyl-2,2'- dicarbocyanine iodide
    - 1,1'-diethyl-4,4'-carbocyanine iodide (also known as cryptocyanine)

Note

The cyanine dyes used in this experiment are toxic irritants. Solutions of these dyes in methanol must be handled wearing gloves at all times. Perform all dilutions in a fume hood. Read the safety data sheets for these dyes (http://www.sigmaaldrich.com) prior to the lab.

Procedure

During the laboratory meeting, your group should use the Group Notebook Template that has been provided in Google Classroom. This template is provided as a guide so that you know what data and information should be kept in a notebook. You may also keep your personal notebook in any way you'd like, but you should translate your notes into this template for the group submission.

A. Prepare the Instrument

To ensure that the instrument is calibrated and functioning well, validate the wavelength accuracy. To do this, perform instrument diagnostics tests using the **Validate** application. (See Operation Instructions for Agilent Cary Spectrophotometers)

B. What energy of light is absorbed?

What are the Experimental λ_{max} from the Dyes' Absorption Spectra?

1. Fill four standard glass cuvettes approximately 4/5 full with methanol (about 2.5 - 3 mL). Then add 3-15 drops of one dye to each cuvette. Add enough dye that you can see a light color for each solution.
2. Use the UV-vis to record the spectrum of each dye. If needed, adjust the solution concentration of one or more of the dye samples until the peak maximum absorbance reading is approximately 0.2 to 1.0 absorbance units.
3. Overlay the spectra of the four dyes. Annotate the resulting overlaid spectra: label each dye spectrum and and label its associated λ_{max} value.
4. Save the samples for steps C and D.

C. Is Beer's Law obeyed under the experimental conditions used?

What is the effect of concentration on the spectrum, and specifically on λ_{max}?

1. Choose one of the four dyes to use as a representative sample.
2. Create two samples in which the concentration of that dye is different by a factor of 2.000 (divide in half or double it). You may use one of the samples from Part B as one of your samples. Perform the sample preparation with precision (use a precise measuring device when doubling or halving concentration) – sloppy work will result in uninterpretable data.
3. Use the UV-vis to record the spectrum of each sample (again, you may use a spectrum from Part B if appropriate).
4. Use the instrument software to create an overlay that shows the effect of concentration on the spectrum. Annotate the spectra to include the name of the dye and the λ_{max} determined at each concentration.

D. Do the dye molecules interact under the experimental conditions used?

What is the effect of mixing on the spectrum, and specifically on each dye's λ_{max} value?

1. Choose two dyes that have λ_{max} values that differ by at least 100 nm.
2. Using the solutions from part B, create a new sample by mixing two of the dyes together in equal volumes.
   **Note that this does not necessarily mean that the concentrations are equal.*
3. Use the UV-vis to record the spectrum.
4. Create an overlay that experimentally demonstrated the effect of mixing. Annotate the spectra to include the names of each sample the λ_{max}'s determined for each sample.

E. Does the Particle in the Box (PIB) model describe the trends in a series of Dyes?

What useful information can we get from experimental data.

1. Use the PIB model to determine the **Effective Box Length (L)**, determine **average C=C bond length** l, and the **lengthening factor (γ)** for the series of dyes (using data from part B).

   Your instructors have prepared a CoLab notebook to help you with this in Google Classroom. **Please go to google classroom if you are enrolled in this course at Duke University.** For other users, the CoLab notebook is freely available here.

2. Compare the average bond length derived from the model to the theoretical bond lengths in benzene. (The value of the average bond length of a carbon-carbon bond in benzene is 1.39 Angtroms.)

Thinking about the Data (Post-Experiment Assignment)

This part of the assignment is where you will solidify and demonstrate your understanding of the theories applied to experimental results. Each question below should be answered thoroughly and clearly in typed text. Your writing should be accurate and grammatically correct. While you may discuss these ideas with your peers, the work submitted for grading must be your own. **Please refer to the Individual ELN Template for the latest version of this assignment.**

A. Tabulate your data.

First, Tabulate your data. An example table is provided:

Dye #	WAVELENGTH (nm)			*For CHEM310 only*		
	λ_{max} Literature*	λ_{max} Experimental		λ_{max} HMO (CHEM310L only)		
	Value ± uncertainty (nm)	Value ± uncertainty (nm)	Absolute Error (nm)	Value (nm)	Absolute Error (nm) compared to experiment	% Error (from exp.)
1	522 ± 1	±		±		
2	605 ± 1	±		±		
3	708 ± 1	±		±		
4	704 ± 1	±		±		
*Fisher, N. I.; Hamer, F. M. A Comparison of the Absorption Spectra of Some Typical Symmetrical Cyanine Dyes. *Proc. A* **1936**, *154* (883), 703–723. https://doi.org/10.1098/rspa.1936.0078.				*You may delete these columns if you are in CHEM301L*		

B. Describe Experimental Data (Results)

- **Compare λ_{max} values to literature:** Reference the table above and assess how your experimental results compare to literature λmax values for each dye. Report all values with appropriate uncertainty and explain how you determined the uncertainty.
- **Experimental trends:** Explain how λ_{max} changes across the dye series in terms of conjugation length and π-electron count.

C. Discuss Beer's Law

- Interpret the effect of concentration and mixing: Explain how dilution and mixing affect λ_{max} of each dye, drawing on the experimental evidence and the theory of Beer's Law to justify your reasoning.
- Compare the experimental results to your initial predictions and explain any discrepancies.

D. PIB Model

- **Evaluate the PIB model:** Assess how well PIB predictions agree with experiment. Use quantitative comparisons to support your evaluation. Report PIB values with appropriate uncertainty and explain how you determined the uncertainty.
- **Justify deviations:** If values differ from predictions or trends, provide evidence-based explanations (structural features, model assumptions, or experimental error).
- **Reflect on models:** Consider the usefulness and limitations of the PIB model. How might more sophisticated models (e.g., Hückel MO) improve predictions?
- **Connect to practice:** Explain how Part I of this experiment illustrates the role of simple models in physical chemistry—what do we gain, and what do we lose, when we rely on approximations.

4.2.1: Instructions for using the UV-Vis Spectrophotometers

4.2.2: Introduction to Particle in the Box (PIB) applied to Dyes

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4.2.1: Instructions for using the UV-Vis Spectrophotometers

Below are the instructions for using the Agilent Cary Series UV-Visible spectrophotometer in the Absorption Spectrum of Conjugated Dyes experiment.

A. Start-up:

Determine which model of UV-vis instrument you are using. Then, confirm that the UV-vis is switched "on".

Agilent Cary 60	Agilent Cary 100
The **Cary 60** instrument has a xenon flash lamp, which does not require warm up.	The **Cary 100** instruments have tungsten and deuterium lamps that must be warmed up for approximately 1 hour prior to use for best results. However, since we are only doing qualitative analysis, it is sufficient for this experiment to warm them up for only a couple of minutes.
How to turn on the Cary 60: The Cary 60 should not be turned off. But, if it is off, check that the cell holders are empty and press the power button on the instrument.	**How to turn on the Cary 100:** With both sample and reference holders empty and the cover closed, turn on the instrument with the switch at the front, lower left. Wait two minutes before proceeding further.
Please leave this Instrument ON when you are finished with your experiment.	*Always power OFF the Cary 100 when you are done for the day!*

B. Validate the Wavelength Accuracy

1. Open the Validation Software by clicking the **Cary WinUV** shortcut on the desktop and selecting the **Validate** application. After a few moments the software screen will appear and will begin to communicate with the instrument. You can follow the progress by monitoring the display at the lower left of the screen. When the traffic light 

in the upper center turns green, the system is ready. You will see absorbance in the upper left and wavelength in the upper right.
2. Open the Validation method used for this course: go to **File** → **Open Method,** navigate to the directory C:\CaryUVvis\Methods, and open the **CHEM301L_Validation.MVD** method file.

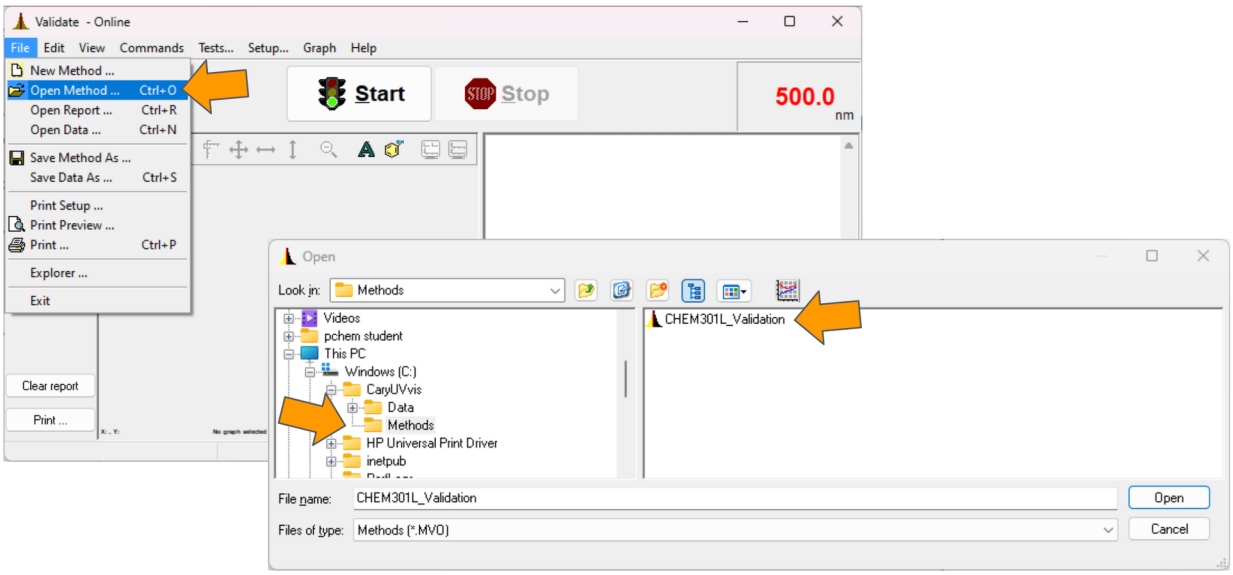


Figure 4.2.1.1: The Validate Main Screen. (CC-NC-BY-DUKE CHEM)

2. Click the Tests ... button to view the Instrument Performance Tests. *Discuss with your instructor which test(s) would be appropriate.* While you could run all of the tests listed, the type of test that is required is a **Wavelength Accuracy** test. There are several options for performing a wavelength accuracy validation. Depending on whether you are using a Cary 100 or a Cary 60, this test can be conducted using either the deuterium (D2) or xenon (Xe) lamp, respectively. Another good option is to use a holmium oxide (Ho_2O_3) standard if one happens to be on hand. **Be sure to state in your notebook which instrument you are using and which specific test is used for the wavelength validation.**

   Using the  button, you can remove all tests from the list except for the Wavelength Accuracy test that you choose to use. The screen should look as shown here, with only the selected text in the list.

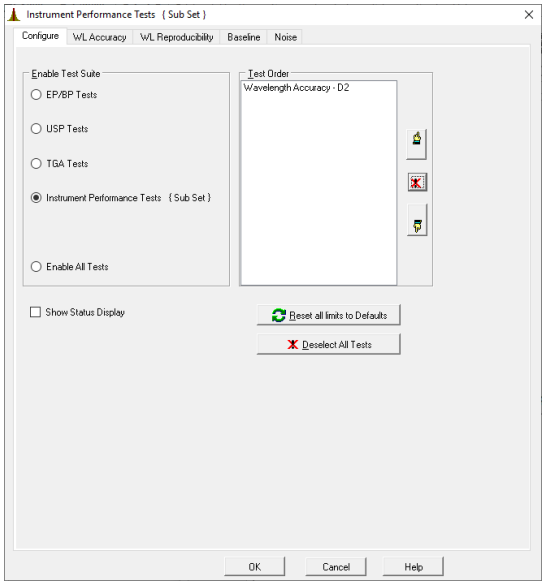


Figure 4.2.1.2: Selecting a Wavelength accuracy test. (CC-NC-BY-DUKE CHEM)

3. Click the Setup ... button and, when the setup screen appears, place your names in the Name line; and, the name of the test in the comments box. In the Options section select Auto Print, Results and Graph. Data Form and Company Logo should not be checked. % Page Height set at 50 is fine.

4. Click 

to return to the main screen.
5. Check the sample compartment to be sure that there are no samples in the instrument and that there is nothing blacking the light path. Gently close the sample compartment.
6. Click Start 

to begin the test. As the test proceeds the spectrum (or spectra) will be displayed. At the conclusion of the test, a report will be generated on the screen. **Include these data in your laboratory notebook**. Check to be sure that the difference between the expected and observed peak positions is one the order of $\pm 0.2 - 0.4$ nm. If it is greater than that, consult your Instructor before proceeding further.

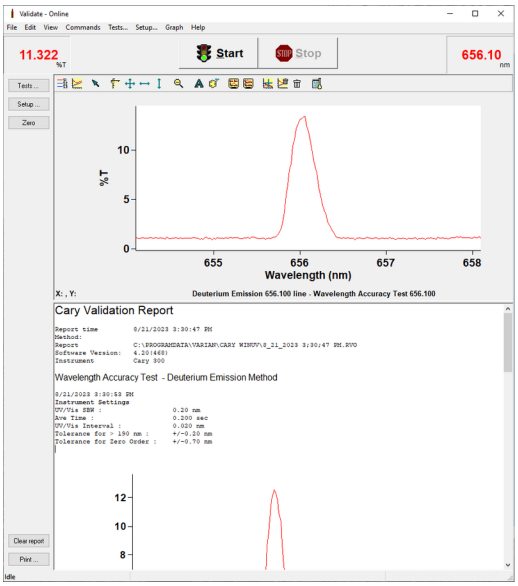


Figure 4.2.1.3: Results of the a Wavelength Accuracy Test using the Deuterium lamp emission on a Cary 100 series spectrophotometer. (CC-NC-BY-DUKE CHEM)

7. Exit the Validation software and return to the Windows Desktop.

C. Setup Scan Application to Collect Absorption Spectra

1. Now, from the **Cary WinUV** list of applications, select the **Scan** application. In a few moments the scan software main screen will appear and will begin to communicate with the instrument. You can follow the progress by monitoring the display at the lower left of the screen. When the traffic light at the top center of the screen turns green, the system is ready. You will see absorbance at the upper left and wavelength at the upper right of the screen.

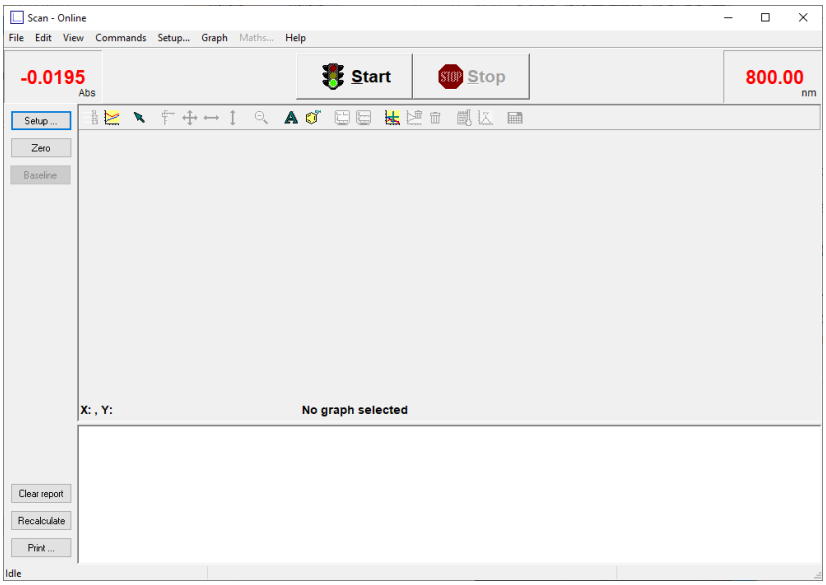


Figure 4.2.1.4: The Scan Module Main Screen. (CC-NC-BY-DUKE CHEM)

2. Click the 

button and wait for the setup screen to appear. Note that the arrangement op options in the setup window depends on which instrument you are using (see Figure below). Begin on the **Cary tab** and in the *Cary Instrument Control Options*, set your scan range from **750 nm to 450 nm**. In the *Scan Controls*, set the **Ave time to 0.1 seconds** and the **Data interval to 1 nm** (on the Cary 60, this is the same as the **Medium** setting). This will yield a Scan Rate of 600 nm/min.

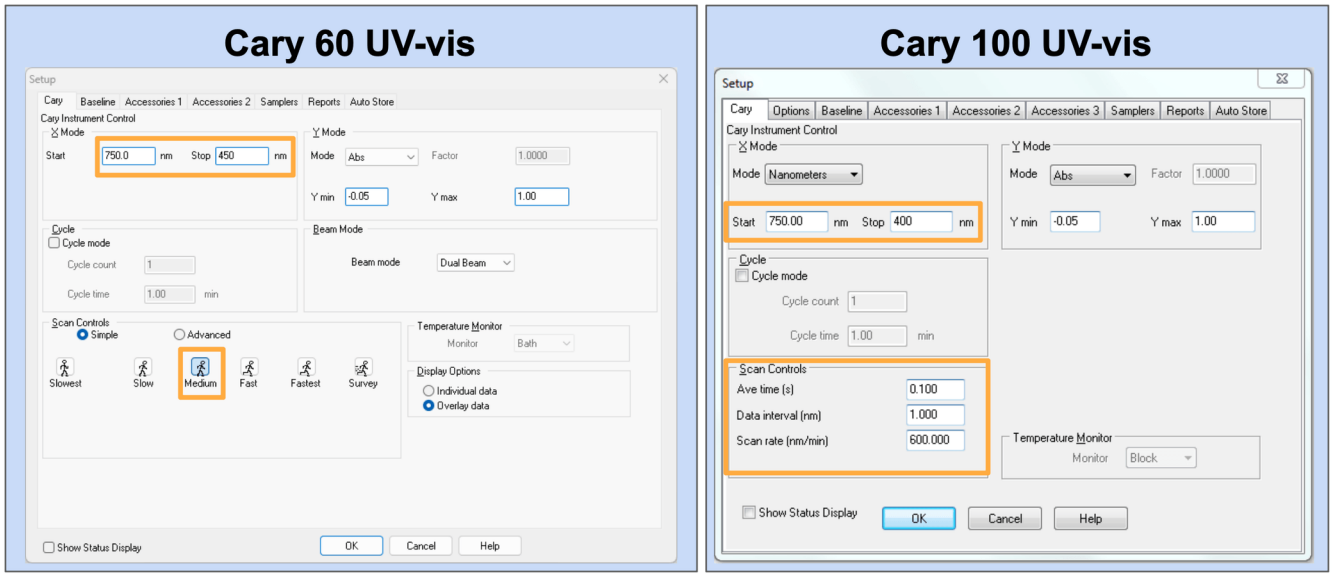


Figure 4.2.1.5: The Scan Setup Widnow, Cary Tab for Cary60 (left) and Cary100 (right) spectrometers. (CC-NC-BY-DUKE CHEM)

3. The default settings are sufficient for most other options. Click on each tab to check that the settings make sense. Particularly for the Baseline Tab, **None** should be selected under *Baseline Selection* settings.

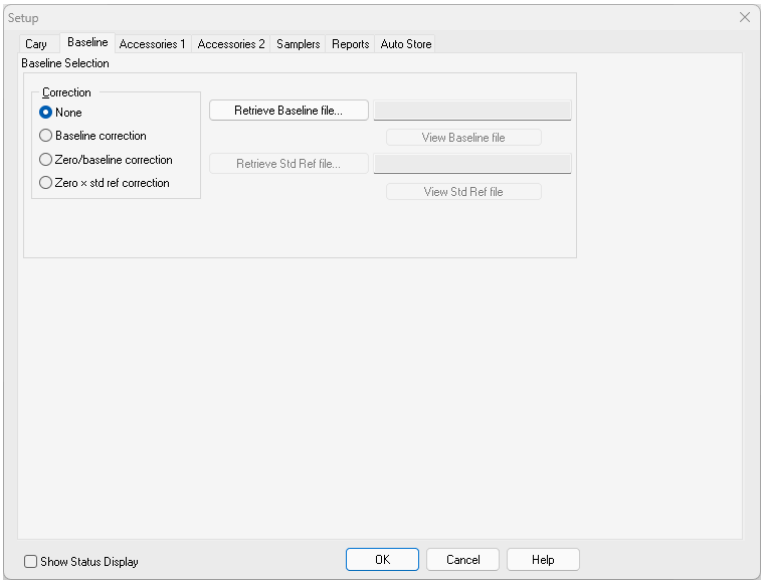


Figure \(\
PageIndex
{6}\): The Baseline Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

4. Finally, select the Reports tab.
   - Put your Section NUmber and Team Number in the Name box.
   - Put the Name of your Experiment, and the names of all team members in the Comment box.
   - Under Peak Table, put a check in All peaks.
   - Be sure the Include XY pairs table is not checked.
   - Click the Peak Information button, and set the Threshold to 0.200. Put Peaks in the Peak Type box.
   - Select for ASCII (csv) in the Autoconvert Option.
   - Click OK to close the Peak information box, and OK again to return to the main screen.

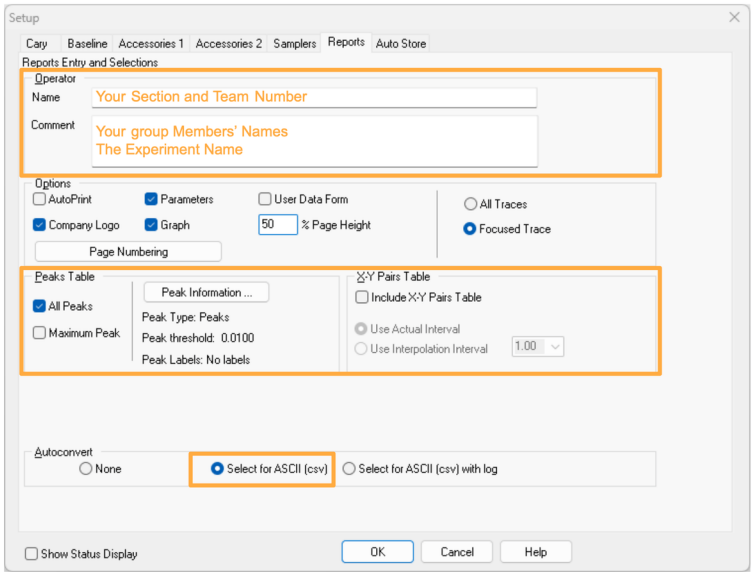


Figure 4.2.1.7: The Reports Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

D. Collect Absorption Spectra

1. Place your first sample in the sample compartment and gently close the cover.

2. Click 

to begin the run.
3. You will be prompted for a filename.
   - Always name your files using the convention **YYYYMMDD_Team@#_X**. Where YYYY is the four-digit year, MM is the two digit number of the month, DD is the two digit day of the month, Team@# is your section day (@) and team number (#), and X is an indicator, like *dyes*. For example, if you are on **W**ednesday, Team **1**, your file name would end with "**TeamW1_dyes**". Since you will be running many samples, give the file the general name appended with a number "_1". *For example, 20260126_TeamW1_Dyes_01.*
   - Save your files in the directory C:\CaryUVvis\Data\current_year\course_semester.
   For example, save in the folder C:\CaryUVvis\data\2026\CHEM301L_Fall26 *if it is Fall 2026 and you are in CHEM301L.*
   - Record where your files are saved and the file names in your notebook (there is a table for this in the template)
4. You will then be prompted for a sample name. Place the name of the sample (Dye_1_two_drops) in this box.
5. As each run proceeds you will see the spectrum generated in real time on the screen. Make sure the maximum absorbance of each sample is between approximately 0.2 and 1.0; adjust the dye concentration to get the absorbance in this range.
6. At the conclusion of each run, place the next sample in the sample compartment and initiate the new scan.
   ****Note**: the software prompts you to enter a filename and/or sample information BEFORE it scans that sample.*

Note

To add or remove traces from the spectrum view, click the  button at the upper left of the toolbar, next to the *Setup* button. Check files to add them or uncheck to remove from the view. Then click Apply or OK.

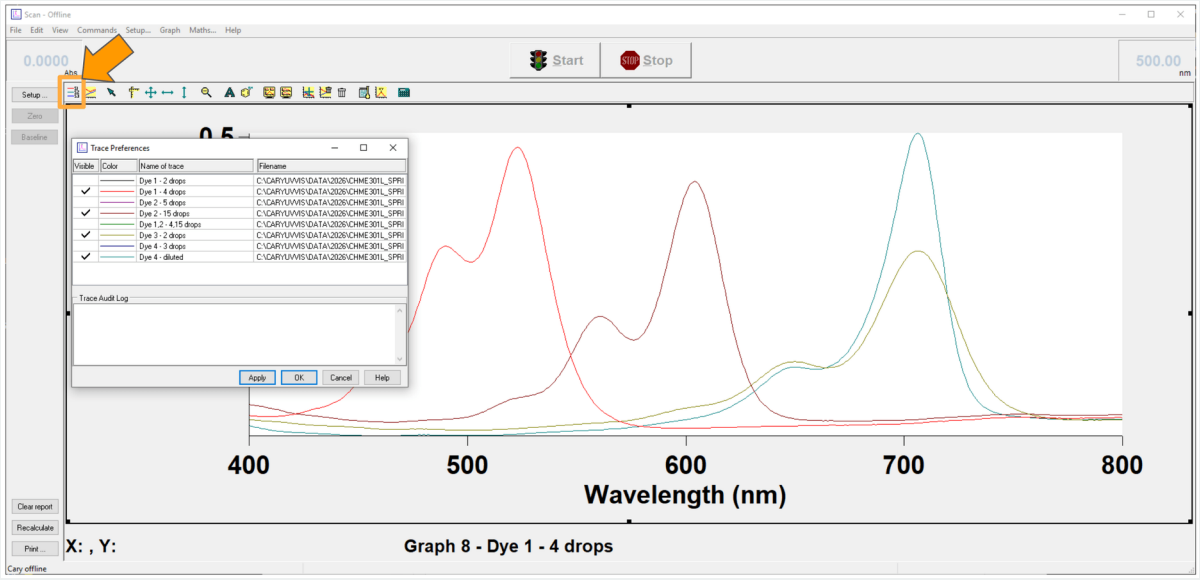


Figure 4.2.1.8: The Absorption Spectra of the Dyes. (Kathryn Haas; CC-NC-BY-SA)

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4.2.2: Introduction to Particle in the Box (PIB) applied to Dyes

Definition: Conjugation

A conjugated π system is one that contains alternating single and double or triple bonds along a chain of carbon atoms. The most common type of conjugation is alternating double and single bonds. A simple example is the butadiene molecule. $H_2C{=}CH{-}CH{=}CH_2$

The Particle-In-A-Box approximation

Electrons in the π-electron system of a conjugated aromatic compound are not restricted to specific nuclei but are free to move throughout the system. In a linear conjugated system the potential energy of the electrons will vary along the chain, being lowest near the nuclei and highest between them. To a first approximation, however, it can be assumed that the potential energy of the electrons is constant along the length of the chain and increases to infinity one bond distance beyond the end atoms of the chain. The electrons may be visualized as being contained in a one-dimensional potential well, of length ℓ, and occupying orbitals of different energy within the well. The wave functions representing the orbitals and the energy levels of the orbitals can be obtained by solving the Schrödinger equation for this system.

For a one-dimensional system the Schrödinger equation takes the form

$$\frac{\partial^2 \psi_{(x)}}{\partial x^2} + \frac{8\pi^2 m}{h^2}\left(E - V\right)\psi_{(x)} = 0 \tag{4.2.2.1}$$

where $\psi_{(x)}$ are wavefunctions that satisfy the equation (eigenfunctions), E is the energy of the particle of mass m, V is the potential energy, and h is Planck's constant.

The potential energy, V, is a constant within the well of length ℓ, where $\psi_{(x)}$ must vanish for $x \leq 0$ and $x \geq \ell$ and $V = \infty$. This allows us to conveniently set V equal to zero in the region $0 \leq x \geq \ell$ when deriving solutions of the equation. The equation then reduces to

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2 \psi_{(x)}}{\partial x^2} = E\psi_{(x)} \tag{4.2.2.2}$$

Solutions of this equation are $\psi_{(x)} = A \cdot \sin\left(\frac{n\pi x}{\ell}\right)$, where A is a constant and n = 1,2,3,... etc.

Verification that this wave function is indeed a solution of the Schrödinger equation may be obtained by substitution into the left- and right-hand sides of the above equation.

$$\begin{aligned}\text{Left-hand side} &= \frac{-h^2}{8\pi^2 m}\left(\frac{-n^2\pi^2}{\ell^2}\right) A \cdot \sin\left(\frac{n\pi x}{\ell}\right) \\ &= \frac{-h^2}{8m\ell^2} A \cdot \sin\left(\frac{n\pi x}{\ell}\right) \\ \text{Right-hand side} &= EA \cdot \sin\left(\frac{n\pi x}{\ell}\right)\end{aligned}$$

The function $\psi_{(x)}$ is a solution of the Schrödinger equation when the energy E of the system has the values $E = \frac{n^2 h^2}{8m\ell^2}$. The allowed energy levels are depicted diagrammatically below.

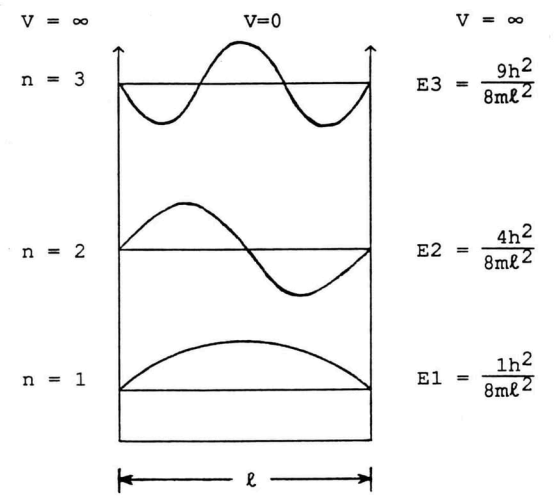


Figure 4.2.2.1: The Particle-in-a-Box Model.

The ground state configuration for the conjugated system of a molecule is derived by allocating two electrons to each of the energy levels in accord with the Pauli exclusion principle. Thus, a molecule with Nπ electrons will have the N/2 lowest levels filled and all the higher levels empty. When the molecule absorbs UV-vis light, the energy absorbed is from an electron in the HOMO (where n = N/2) becoming excited to the LUMO where n = (N/2) + 1. The energy change, ΔE, for this transition is

$$\begin{aligned}\Delta E &= E_{\left(\frac{N}{2}+1\right)} - E_{\left(\frac{N}{2}\right)} \\ &= \frac{\left[\left(\frac{N}{2}\right)+1\right]^2 h^2}{8m\ell^2} - \frac{\left(\frac{N}{2}\right)^2 h^2}{8m\ell^2} \\ &= \frac{(N+1)\,h^2}{8m\ell^2}\end{aligned}$$

Since $\Delta E = h\nu = \frac{hc}{\lambda}$ where c is the speed of light and λ is the wavelength, then

$$\lambda = \frac{8mc}{h}\frac{\ell^2}{(N+1)} \tag{4.2.2.3}$$

Thus if ℓ is known, this relation can be used to calculate the wavelength maximum of the band representing the transition from the ground state to the first excited state in a π-electron system.

PIB model for cyanine dyes:

This Particle-in-th-Box model can be applied to carbocyanine dyes which may be represented, for example, by the resonance forms shown below for the 1,1'- diethyl-4,4'-carbocyanine (cryptocyanine) cation.

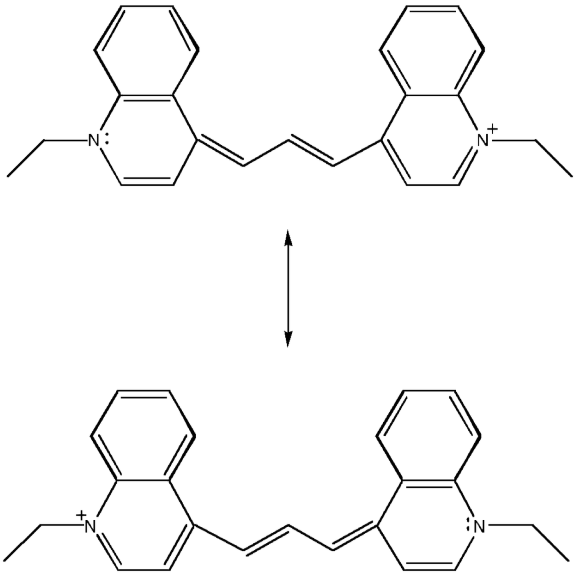


Figure 4.2.2.2: The *1,1'-Diethyl-4,4'-carbocyanine (cryptocyanine) cation*. (CC-NC-BY-DUKE CHEM)

The π-electrons in the molecule are regarded as a collection of "free" electrons (independent particles) confined to a box, whose wavefunctions are the square-well functions. Once again, these electrons are distributed among the wavefunctions and energy levels according to Pauli principles, so that the absorption of energy (light) according to this model will follow equation 4.2.2.3. To apply the model to the absorbance λ of a specific molecule we need to determine N (number of \pi electrons) and ℓ (length of the conjugated chain).

Number of π electrons in cyanine dyes (N): In the chain between the two nitrogen atoms, each carbon atom contributes one π electron. The π system also includes a total of three additional electrons contributed from the N atoms. Two of these electrons are contributed from the neutral N, while one is contributed from the cationic nitrogen (assuming the resonance structures shown in Figure 4.2.2.2). If we denote the number of carbon atoms in the polymethine chain (between the two nitrogen atoms) by p, then N, the number of π-electrons, is p + 3.

$$N = p + 3 \tag{4.2.2.4}$$

Where N is the number of π electrons in the system, and p is the number of carbon atoms between the nitrogen atoms.

Approximation of ℓ in cyanine dyes: The total length of the potential well is taken to be the length of the shortest carbon chain between the nitrogen atoms *plus one bond length at each end*. Assuming that the length of one bond is 1.39×10^{-8} cm, an approximation for ℓ is

$$\ell = (p + 3)a \tag{4.2.2.5}$$

where $a = 1.39x10^{-8}$ cm is the mean distance between atoms in the chain.

PIB model for Cyanine Dyes: Substituting 4.2.2.4 for N and 4.2.2.5 for ℓ in equation 4.2.2.3 yields:

$$\lambda = \frac{8mca^2}{h}\frac{(P+3)^2}{P+4} \tag{4.2.2.6}$$

If polarizable groups are present at the ends of the chain, then the potential energy of the π-electrons in the chain does not rise so steeply at the ends. This results in lengthening of the box length, ℓ, which can be incorporated into equation 4.2.2.6 through the addition of a new "lengthening" parameter, γ, resulting in

$$\lambda = \frac{8mca^2}{h}\frac{(P+3+\gamma)^2}{P+4} \tag{4.2.2.7}$$

where γ should be a constant for a series of dyes of a given type and should lie between 0 and 2. If such a series is studied experimentally, the empirical parameter γ may be adjusted to achieve the best fit to the data.

The Hückel Molecular Orbital (HMO) model

The molecular orbital (MO) energy level diagrams of a conjugated π- system can be constructed using a set of approximations suggested by Erich Hückel. The Hückel Molecular Orbital (HMO) method is not traditionally approached as an ab-initio quantum calculation (from theory alone), but is usually used as an empirical method (includes experimental data) for doing quantum calculations. This means that some number of adjustable parameters appear in the theory, and these parameters are determined by comparison with experiment (such as the electronic spectra of dye molecules). If the theory is successful, it can be used to predict the spectra and properties of other conjugated systems once the values of the adjustable parameters have been set for some set of reference compounds.

The Hückel model assumes that a π-molecular orbital, Ψ, delocalized over n atoms can be written as a linear combination of n atomic orbitals (LCAO) ϕ_i

$$\Psi = \sum_i c_i \phi_i \tag{4.2.2.8}$$

where the ϕ_i's are the atomic p_z orbitals on the atoms i (z is perpendicular to the molecular plane). The corresponding one-electron π density at atom i is given by

$$\rho_{i\pi} = c_i^2 \tag{4.2.2.9}$$

The energy E and the coefficients c_i for the ground state are determined by use of the *variation principle*, which says that one should choose the coefficients such that

$$E = \frac{\int \Psi H \Psi d\tau}{\Psi^2 d\tau} = minimum \tag{4.2.2.10}$$

Here the Hamiltonian, H, is an effective one-electron energy operator whose explicit form need not be specified in the empirical HMO approach. The variation principle ensures that the lowest-energy state is as close as possible to the true energy, and the coefficients are obtained from the minimization relations

$$\frac{\partial E}{\partial c_i} = 0; \quad i = 1 \ldots n \tag{4.2.2.11}$$

This results in n equations of the form

$$\begin{array}{cccc} c_1 (H_{11} - S_{11}E) + & c_2 (H_{12} - S_{12}E) + & \ldots & c_n (H_{1n} - S_{1n}E) = 0 \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ c_1 (H_{n1} - S_{n1}E) + & c_2 (H_{n2} - S_{n2}E) + & \ldots & c_n (H_{nn} - S_{nn}E) = 0 \end{array} \tag{4.2.2.12}$$

In these equations, $H_{ii} = \int \phi_i H \phi_i d\tau \equiv \alpha_i$, called the ***Coulomb integral***, is the energy of an electron in a 2p orbital on atom i, while $H_{ij} = \int \phi_i H \phi_j d\tau \equiv \beta_{ij}$, the *resonance* or ***bond integral***, represents the interaction energy of two atomic orbitals on atoms i and j. Both α_i and β_{ij} are negative energy quantities. $S_{ij} = \int \phi_i \phi_j d\tau$ is the overlap integral, which, in the simplest approximation, is taken to be 1 if i = j, and 0 otherwise. For a π system involving only carbon atoms, $\alpha_i \equiv \alpha$ and Equations 4.2.2.12 take the form

$$\begin{array}{cccc} c_1 (\alpha - E) + & c_2 \beta_{12} + & \ldots & c_n \beta_{1n} = 0 \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ c_1 \beta_{n1} + & c_2 \beta_{n2} + & \ldots & c_n (\alpha - E) = 0 \end{array} \tag{4.2.2.13}$$

These equations have a nontrivial solution only if the corresponding ***secular determinant*** vanishes:

$$\begin{vmatrix} \alpha - E & \beta_{12} & \dots & \beta_{1n} \\ . & & & . \\ . & & & . \\ . & & & . \\ \beta_{n1} & \beta_{n2} & \dots & \alpha - E \end{vmatrix} = 0 \tag{4.2.2.14}$$

The HMO method makes several simplifying assumptions. The first of these are as follows:

1. The π-orbitals are considered separately from the σ-orbitals. The σ-orbitals only enter indirectly in so far as they determine the geometry of the molecule.

2. Treat all the carbon atoms as identical. This means that all the Coulomb integrals (α) are equal.

The next stage is to express the π-orbitals as LCAOs of the C2p-orbitals, ϕ. In ethene (CH_2=CH_2) we would write

$$\Psi = c_A(\phi_A) + c_B(\phi_B) \tag{4.2.2.15}$$

and in butadiene (H_2C=CH−CH=CH_2)

$$\Psi = c_A(\phi_A) + c_B(\phi_B) + c_C(\phi_C) + c_D(\phi_D) \tag{4.2.2.16}$$

The optimum coefficients and energies are found by the variation principle. This involves solving the secular determinant, equation (Appendix B.7), which for ethene would be

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{4.2.2.17}$$

and its roots are $E = \alpha \pm \beta$. The state with energy $\alpha + \beta$ corresponds to the bonding combination (β is negative) and $\alpha - \beta$ corresponds to the antibonding combination, Figure 4.2.2.1.

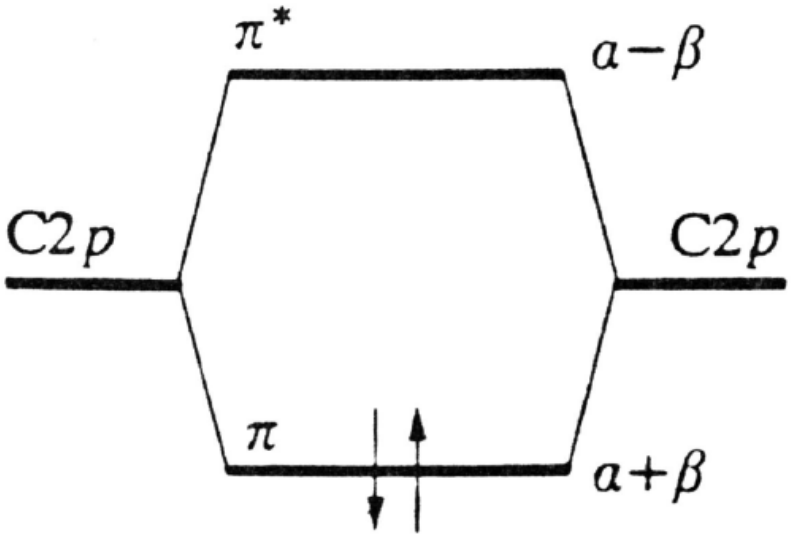


Figure 4.2.2.1: The Hückel Molecular Orbital Energy Levels of Ethene. Two electrons occupy the lower π-*orbital*. (CC-NC-BY-DUKE CHEM)

Each carbon atom supplies one electron to the π-system and the bonding orbital is occupied by an electron pair. The π-electronic energy of ethene is therefore $2\alpha + 2\beta$. The excited state of the molecule, when an electron is excited into the π^*-orbital, lies about 2β above the ground state.

In the case of butadiene, the approximations result in the determinant

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{4.2.2.18}$$

This expands into the quadratic equation

$$x^4 - 3x^2 + 1 = 0; \quad x = \frac{(\alpha - E)}{\beta} \tag{4.2.2.19}$$

with roots x^2 = 2.62, 0.38. Therefore, the energies of the four LCAO-MOs are

$$E = \alpha \pm 1.62\beta \quad and \quad E = \alpha \pm 0.62\beta \tag{4.2.2.20}$$

as shown in Figure 4.2.2.2. There are four electrons to accommodate, and so the ground state configuration is $1\pi^2 2\pi^2$.

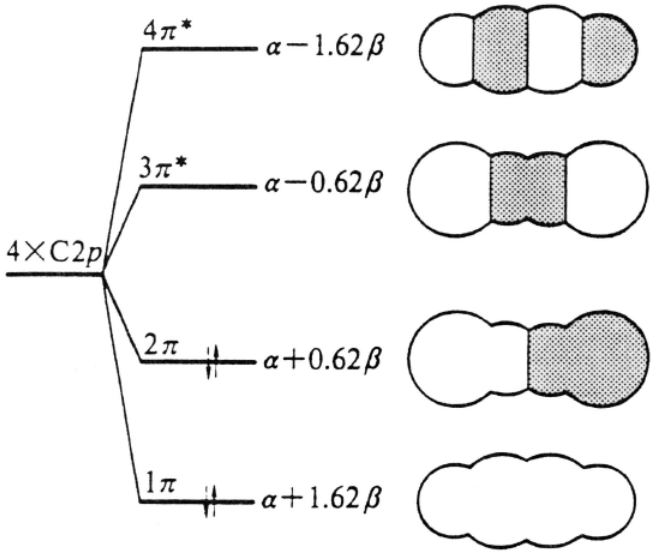


Figure 4.2.2.2: The Hückel molecular orbital energy levels of butadiene and the top view of the corresponding π-orbitals. The four p-electrons (one supplied by each carbon atom) occupy the two lower (\pi \)-orbitals. Note that the orbitals are delocalized. (CC-NC-BY-DUKE CHEM)

An important point emerges when we calculate the total π-electron binding energy in butadiene and compare it with what we find in ethene. In ethene the total energy is $2(\alpha + \beta) = (2\alpha + 2\beta)$; in butadiene it is $2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = (4\alpha + 4.48\beta)$. Therefore, the energy of the butadiene molecule lies lower by $(4\alpha + 4.48\beta) - 2(2\alpha + 2\beta) = 0.48\beta$ (roughly –36 kJ mol^{-1}) than the sum of two π-bonds. This extra stabilization of a conjugated system is called the ***delocalization energy.***

To obtain the wavefunction for a given energy state, E_j, one substitutes E = E_j into Equation 4.2.2.13 and solves for the jth set of coefficients c_{j1}, c_{j2}, ..., c_{jn}. This process actually gives only ratios of coefficients; to determine numerical values, we add the normalization condition

$$\int \Psi_j^2 d\tau = \sum_i c_{ij}^2 = 1 \tag{4.2.2.21}$$

The four Hückel molecular orbitals for 1,3-butadiene are

$$\begin{aligned} \Psi_1 &= 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \\ \Psi_2 &= 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4 \\ \Psi_3 &= 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4 \\ \Psi_4 &= 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4 \end{aligned} \tag{4.2.2.22}$$

In addition to π-electron energies and wavefunctions, the HMO approach also allows one to calculate several other quantities of chemical interest, such as electron densities, bond orders and free valence.

Heteroatoms

Heteroatoms (X) may be incorporated in the HMO method by appropriate changes in the empirical α and β parameters associated with each atom and bond. A common example would be the inclusion of the π-electron contribution from the nitrogen atom in pyridine. These changes are incorporated in units of the standard α_0 and β_0, usually of benzene, by use of the definitions

$$\alpha_X = \alpha_0 + h_X \beta_0 \tag{4.2.2.23}$$

$$\beta_{CX} = k_{CX} \beta_0 \tag{4.2.2.24}$$

Calculations involving such changes can be made by solving the secular equations. Unfortunately there remains considerable controversy concerning the specific values to be used for the h and k-parameters of various heteroatoms. Part of the problem is that there are several variations of MO theory and each will yield somewhat different parameter values with a given application.

We should distinguish, for example, the nitrogen in pyridine from a pyridinium nitrogen. In the former case, the heteroatom contributes two electrons to the π-system; in the latter case it contributes one. In the second part of the analysis of your experimental data, you will use a "canned" HMO computer program to determine the energy levels and molecular orbitals of the π-states of the dye molecules (as a function of β). By comparison of these results with your experimental data, you will determine an empirical value for β. Note that this program incorporates values for the heteroatom parameters h and k. You will need only to specify the location and type (e.g., pyridine-type nitrogen) of each heteroatom in the molecule to be studied.

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4.3: PROCEEDURE (PART II) – HÜCKEL CALCULATIONS USING HULIS (PART II)

The ELN template for this part of the experiment is here: ELN01_2_Huckle2022.docx

Huckle Calculation Tasks

Perform the tasks listed here using the instructions for using Hulis that are given below.

1. Perform Huckle Molecular Orbital (HMO) calculations for each of the four dyes. In the HMO analysis, omit the ethyl groups since they are not part of the conjugated network. Save a screen-shot image of the entire program window showing the structure and the orbital diagram before moving on to the next one.
2. Calculate the energy difference, ΔE, between the HOMO and LUMO levels (in terms of β) for each dye.
3. Plot the experimentally observed ΔE's (kJ/mol) (from UV-vis in Part I, plot as y or ordinate) vs the calcuated HMO ΔE's (abscissa or x).
   a. From the least-squares slope of the resultant line, determine a semiempirical value for β (β is the spectroscopic exchange integral). Report the uncertainty in β.
   b. Compare your derived value of β with the accepted range for this constant (a.k.a spectroscopic exchange integral), which is – 250 to – 350 kJ/mole.[9]
4. Use your value of β to calculate the energy difference, ΔE, between the HOMO and LUMO levels in units of kJ/mol and eV for each dye. Using these energies, calculate the wavelength (nm) at which you would expect to observe this HOMO → LUMO transition for each dye, using the HMO model.
5. Calculate the percent error between your calculated HMO results your experimental values. Tabulate your data in the format shown below.

	WAVELENGTH (nm)						
Dye #	λ_{max} Literature*	λ_{max} Experimental		λ_{max} Particle-in-box		λ_{max} HMO	
		Value (nm)	Absolute Error (nm)	Value (nm)	% Error (from exp.)	Value (nm)	% Error (from exp.)
		±					
		±					
		±					
		±					

* reference for your literature values goes here

6. Use this table as the basis for discussion of your results. Which theoretical model gives the best fit to the experimental data, and why? Are the results for each dye equally satisfactory? If your answer is no, explain why you think this is so. How are these models useful and what might be done to improve the results?
7. Calculate the wavelength (nm) and minimum excitation energy (eV) of the molecule CH2=CHCH=CHCH=CHCH=CH2 using the HMO model program. In calculation use your value of β to convert to electron volts. What color does the molecule absorb from white light? What color does it then appear?

Instructions For Using The Program "Hulis" ver. 3.0.x

Note

Hulis is a Java applet. Java must be installed to run the applet. You are welcome to run it from your own laptop if Java is installed. But for your convenience in the event that you do not want Java on your computer, the program is available on all of the lab computers.

Hulis and Java can be downloaded here: Huckel Theory and HuLis

1. Double-click on the Hulis icon to Start the Program
2. Running the Program:
   The main screen shows a molecule builder. Highlight **Build** on the left side of the screen if it is not already highlighted when the program starts.

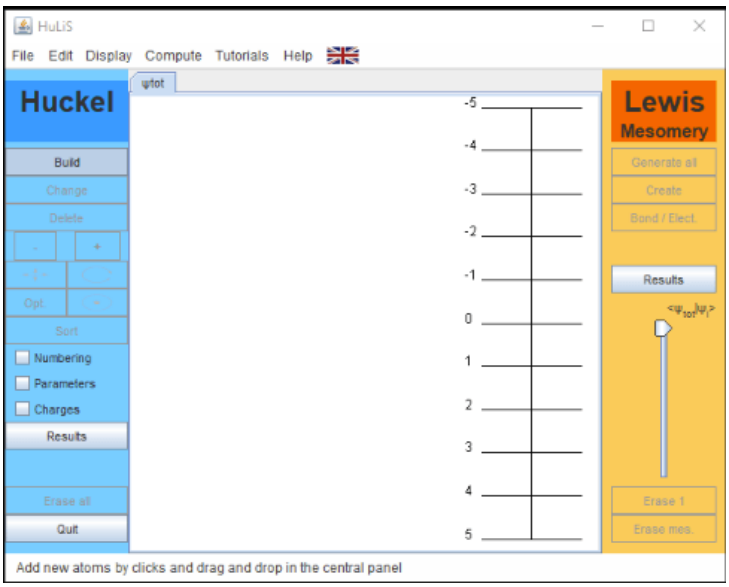
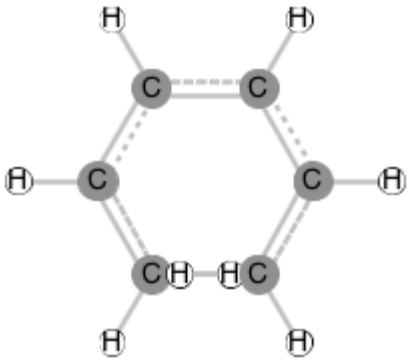
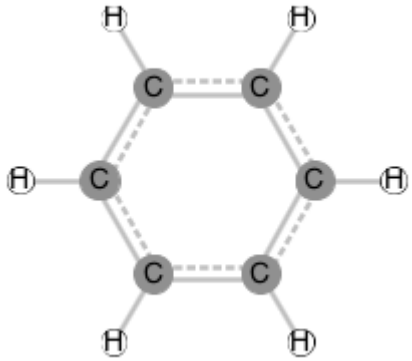


Figure 4.3.1: The Hulis Main Screen. (CC-NC-BY-DUKE CHEM)

To build a molecule, for example, Dye 1, begin by clicking anywhere in the blank window in the center of the screen. A CH_3 group should appear. Click on one of the available hydrogens to add a conjugated carbon to your molecule. As you add carbons to form the first ring, you will see the orbital diagram for the molecule appear in the right-hand panel of the program.



You can follow the electron count from this pane of the program window. After putting 6 carbons to form the ring, you will need to form a bond between the two open and adjacent carbons. To do this, simply click on one of the open carbons and drag a bond over to the adjacent open carbon. The hydrogens will disappear and a delocalized C-C bond will form.



3. Continue adding carbon atoms as appropriate to form the template molecule. When you are done your structure will look like this:

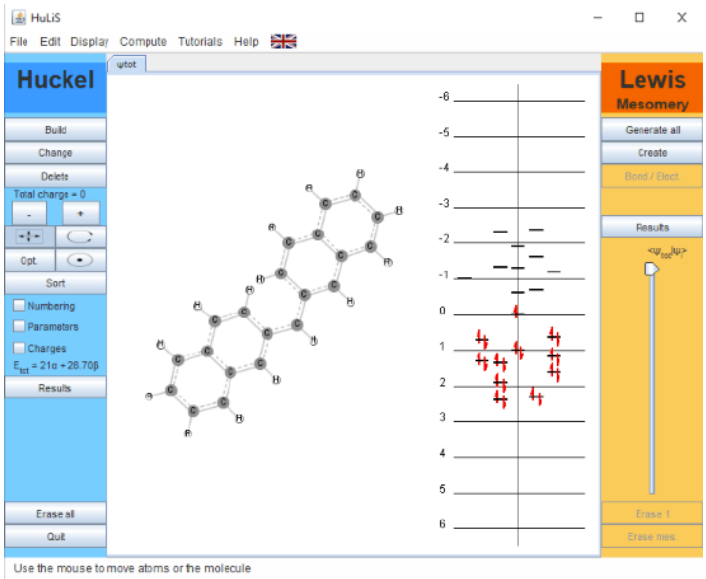
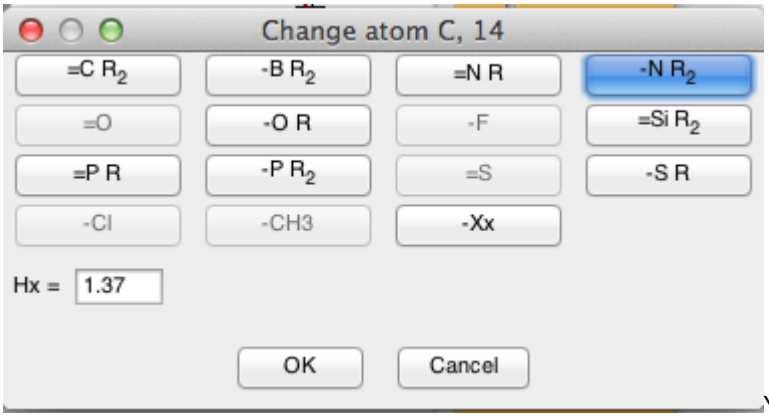


Figure 4.3.2: Dye 1. Note that for the purposes of a Hückel calculation the ethyl groups are omitted (CC-NC-BY-DUKE CHEM)

Note

You can rescale the display on the screen using Zoom out from the Display menu. You can also move, rotate, and center the molecule in the display window with the appropriate control buttons in the left-hand (blue colored) pane of the program window. In the image above the Move button is currently highlighted.



4. You now need to change two of the carbon atoms to nitrogen to complete the structure. Click on the Change button in the left-hand pane, and then double-click on the appropriate carbon in your structure. A Change Atom box appears. Select =NR to change this to the pyridinium group. Check to be sure the value in the Hx box = 0.51. Click on OK. Now change the other carbon to a nitrogen in the same way, but this time select the –NR2 option. Be Sure the value in the Hx box = 1.37. Click OK. Finally, make the molecule a cation by clickingh the + in the left-hand pane to increase the Total charge to 1. You final molecule will look as shown below.

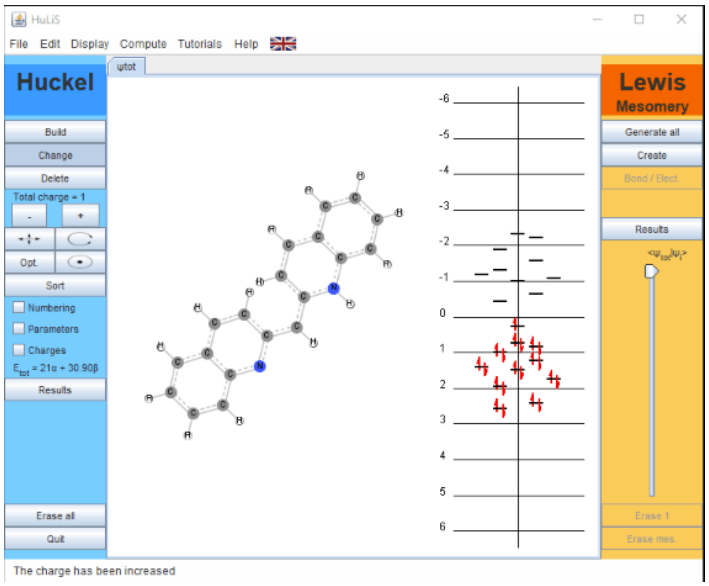
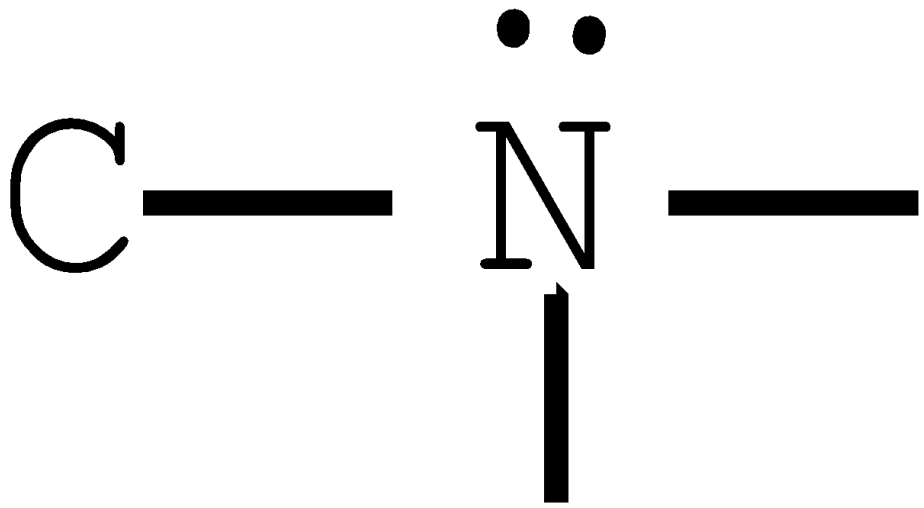
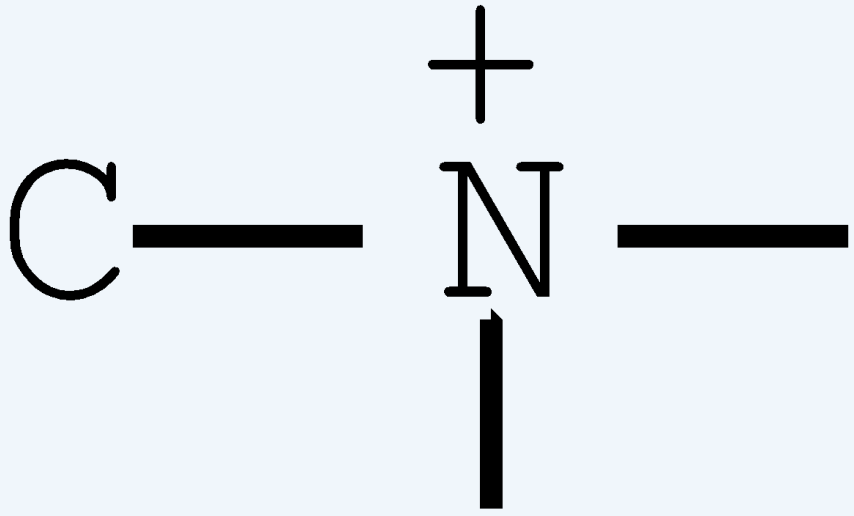


Figure 4.3.3: 1,1'-Diethyl-2,2'-Cyanine Iodide. The ethyl groups are omitted to simplify the calculations. (CC-NC-BY-DUKE CHEM)

Looking at the orbital diagram in the right-hand (orange) pane of the program screen you will see the occupied and unoccupied orbitals, as calculated by the simple Hückel approximation. You can see that the 21 pi-electrons in the molecule occupy the first 11 pi-orbitals; the HOMO to LUMO transition occurs between the 11th and 12th pi-orbital.

5. Click on the Results button, and a Results window appears with significant information about the Hückel calculation. Please note the following things:
   a. As you scan down the Hamiltonian matrix check to see that the Coulomb and Exchange integrals for heteroatoms and carbon-to-heteroatom bonds are as shown in the table below. If you need to see how your atoms are numbered in your structure to make it easier to find them in the Result table, put a check in the Numbering box in the left hand pane of the program window.

Atom	Bond		Nu of p- Ele
C	C=C		1
N		Pyridine	2
N		Pyridinium	1

b. In the Orbitals section of the Results box count over the appropriate number of orbitals (11 in the case of Dye 1), and record the results for the HOMO and LUMO in this molecule.

2- Orbitals :					
εi :	α + 2.5600β	α + 2.4065β	α + 1.9386β	α + 1.7503β	α + 1.4876β
α + 1.3928β	α + 1.2322β	α + 1.0000β	α + 0.8229β	α + 0.7227β	α + 0.2737β
α - 0.4390β	α - 0.6513β	α - 1.0000β	α - 1.0928β	α - 1.1960β	α - 1.3237β
α - 1.5793β	α - 1.8803β	α - 2.2244β	α - 2.3204β		

Figure 4.3.4: Orbital Energies for Dye 1. (CC-NC-BY-DUKE CHEM)

Notice that in this case the energy of the HOMO is $\alpha + 0.2737\beta$; and, the energy of the LUMO is $\alpha - 0.4390\beta$.

> **Note**
>
> **NOTE**: you can change the number of digits in the display from **Preferences**, under the **File** menu.

Close the Results Box.

c. To get a visual representation of the pi-molecular orbitals generated in the Hückel program, simply click on one of the orbitals in the right-hand pane of the program window. The orbital will appear on top of the molecule in the main screen. The image below is of the HOMO.

   You can turn off the orbital display from your molecule by clicking below the orbitals in the right-hand pane of the program window. Save a screen-shot image of the entire program window showing the structure and the orbital diagram.

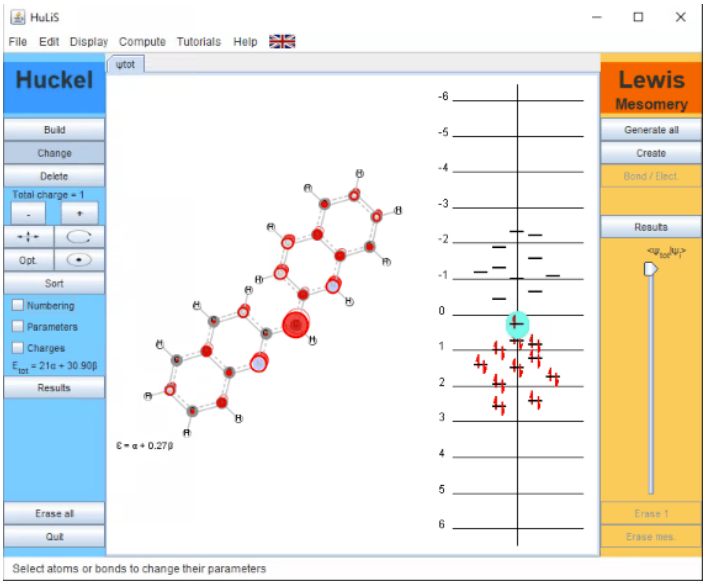


Figure 4.3.5: The Highest Occupied Molecular Orbital in Dye 1. (CC-NC-BY-DUKE CHEM)

4.3.1: Introduction to Hückel Theory

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4.3.1: Introduction to Hückel Theory

The molecular orbital (MO) energy level diagrams of a conjugated π- system can be constructed using a set of approximations suggested by Erich Hückel. The Hückel Molecular Orbital (HMO) method is not traditionally approached as an ab-initio quantum calculation (from theory alone), but is usually used as an empirical method (includes experimental data) for doing quantum calculations. This means that some number of adjustable parameters appear in the theory, and these parameters are determined by comparison with experiment (such as the electronic spectra of dye molecules). If the theory is successful, it can be used to predict the spectra and properties of other conjugated systems once the values of the adjustable parameters have been set for some set of reference compounds.

The Hückel model assumes that a π-molecular orbital, Ψ, delocalized over n atoms can be written as a linear combination of n atomic orbitals (LCAO) ϕ_i

$$\Psi = \sum_i c_i \phi_i \tag{4.3.1.1}$$

where the ϕ_i's are the atomic p_z orbitals on the atoms i (z is perpendicular to the molecular plane). The corresponding one-electron π density at atom i is given by

$$\rho_{i\pi} = c_i^2 \tag{4.3.1.2}$$

The energy E and the coefficients c_i for the ground state are determined by use of the *variation principle*, which says that one should choose the coefficients such that

$$E = \frac{\int \Psi H \Psi d\tau}{\Psi^2 d\tau} = minimum \tag{4.3.1.3}$$

Here the Hamiltonian, H, is an effective one-electron energy operator whose explicit form need not be specified in the empirical HMO approach. The variation principle ensures that the lowest-energy state is as close as possible to the true energy, and the coefficients are obtained from the minimization relations

$$\frac{\partial E}{\partial c_i} = 0; \quad i = 1 \ldots n \tag{4.3.1.4}$$

This results in n equations of the form

$$\begin{array}{cccc} c_1 (H_{11} - S_{11}E) + & c_2 (H_{12} - S_{12}E) + & \ldots & c_n (H_{1n} - S_{1n}E) = 0 \\ . & & & . \\ . & & & . \\ . & & & . \\ c_1 (H_{n1} - S_{n1}E) + & c_2 (H_{n2} - S_{n2}E) + & \ldots & c_n (H_{nn} - S_{nn}E) = 0 \end{array} \tag{4.3.1.5}$$

In these equations, $H_{ii} = \int \phi_i H \phi_i d\tau \equiv \alpha_i$, called the ***Coulomb integral***, is the energy of an electron in a 2p orbital on atom i, while $H_{ij} = \int \phi_i H \phi_j d\tau \equiv \beta_{ij}$, the *resonance* or ***bond integral***, represents the interaction energy of two atomic orbitals on atoms i and j. Both α_i and β_{ij} are negative energy quantities. $S_{ij} = \int \phi_i \phi_j d\tau$ is the overlap integral, which, in the simplest approximation, is taken to be 1 if i = j, and 0 otherwise. For a π system involving only carbon atoms, $\alpha_i \equiv \alpha$ and Equations 4.3.1.5 take the form

$$\begin{array}{cccc} c_1 (\alpha - E) + & c_2 \beta_{12} + & \ldots & c_n \beta_{1n} = 0 \\ . & & & . \\ . & & & . \\ . & & & . \\ c_1 \beta_{n1} + & c_2 \beta_{n2} + & \ldots & c_n (\alpha - E) = 0 \end{array} \tag{4.3.1.6}$$

These equations have a nontrivial solution only if the corresponding ***secular determinant*** vanishes:

$$\begin{vmatrix} \alpha - E & \beta_{12} & \dots & \beta_{1n} \\ . & & & . \\ . & & & . \\ . & & & . \\ \beta_{n1} & \beta_{n2} & \dots & \alpha - E \end{vmatrix} = 0 \tag{4.3.1.7}$$

The HMO method makes several simplifying assumptions. The first of these are as follows:

1. The π-orbitals are considered separately from the σ-orbitals. The σ-orbitals only enter indirectly in so far as they determine the geometry of the molecule.

2. Treat all the carbon atoms as identical. This means that all the Coulomb integrals (α) are equal.

The next stage is to express the π-orbitals as LCAOs of the C2p-orbitals, ϕ. In ethene (CH_2=CH_2) we would write

$$\Psi = c_A(\phi_A) + c_B(\phi_B) \tag{4.3.1.8}$$

and in butadiene (H_2C=CH−CH=CH_2)

$$\Psi = c_A(\phi_A) + c_B(\phi_B) + c_C(\phi_C) + c_D(\phi_D) \tag{4.3.1.9}$$

The optimum coefficients and energies are found by the variation principle. This involves solving the secular determinant, equation (Appendix B.7), which for ethene would be

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{4.3.1.10}$$

and its roots are $E = \alpha \pm \beta$. The state with energy $\alpha + \beta$ corresponds to the bonding combination (β is negative) and $\alpha - \beta$ corresponds to the antibonding combination, Figure 4.3.1.1.

Figure 4.3.1.1: The Hückel Molecular Orbital Energy Levels of Ethene. Two electrons occupy the lower π-*orbital*. (CC-NC-BY-DUKE CHEM)

Each carbon atom supplies one electron to the π-system and the bonding orbital is occupied by an electron pair. The π-electronic energy of ethene is therefore $2\alpha + 2\beta$. The excited state of the molecule, when an electron is excited into the π^*-orbital, lies about 2β above the ground state.

In the case of butadiene, the approximations result in the determinant

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{4.3.1.11}$$

This expands into the quadratic equation

$$x^4 - 3x^2 + 1 = 0; \quad x = \frac{(\alpha - E)}{\beta} \tag{4.3.1.12}$$

with roots x^2 = 2.62, 0.38. Therefore, the energies of the four LCAO-MOs are

$$E = \alpha \pm 1.62\beta \quad and \quad E = \alpha \pm 0.62\beta \tag{4.3.1.13}$$

as shown in Figure 4.3.1.2. There are four electrons to accommodate, and so the ground state configuration is $1\pi^2 2\pi^2$.

Figure 4.3.1.2: The Hückel molecular orbital energy levels of butadiene and the top view of the corresponding π-orbitals. The four p-electrons (one supplied by each carbon atom) occupy the two lower (\pi \)-orbitals. Note that the orbitals are delocalized. (CC-NC-BY-DUKE CHEM)

An important point emerges when we calculate the total π-electron binding energy in butadiene and compare it with what we

find in ethene. In ethene the total energy is $2(\alpha+\beta)=(2\alpha+2\beta)$; in butadiene it is $2(\alpha+1.62\beta)+2(\alpha+0.62\beta)=(4\alpha+4.48\beta)$. Therefore, the energy of the butadiene molecule lies lower by $(4\alpha+4.48\beta)-2(2\alpha+2\beta)=0.48\beta$ (roughly –36 kJ mol^{-1}) than the sum of two π-bonds. This extra stabilization of a conjugated system is called the ***delocalization energy.***

To obtain the wavefunction for a given energy state, E_j, one substitutes E = E_j into Equation 4.3.1.6 and solves for the jth set of coefficients c_{j1}, c_{j2}, ..., c_{jn}. This process actually gives only ratios of coefficients; to determine numerical values, we add the normalization condition

$$\int \Psi_j^2 d\tau = \sum_i c_{ij}^2 = 1 \tag{4.3.1.14}$$

The four Hückel molecular orbitals for 1,3-butadiene are

$$\begin{aligned}
\Psi_1 &= 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \\
\Psi_2 &= 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4 \\
\Psi_3 &= 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4 \\
\Psi_4 &= 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4
\end{aligned} \tag{4.3.1.15}$$

In addition to π-electron energies and wavefunctions, the HMO approach also allows one to calculate several other quantities of chemical interest, such as electron densities, bond orders and free valence.

Heteroatoms

Heteroatoms (X) may be incorporated in the HMO method by appropriate changes in the empirical α and β parameters associated with each atom and bond. A common example would be the inclusion of the π-electron contribution from the nitrogen atom in pyridine. These changes are incorporated in units of the standard α_0 and β_0, usually of benzene, by use of the definitions

$$\alpha_X = \alpha_0 + h_X\beta_0 \tag{4.3.1.16}$$

$$\beta_{CX} = k_{CX}\beta_0 \tag{4.3.1.17}$$

Calculations involving such changes can be made by solving the secular equations. Unfortunately there remains considerable controversy concerning the specific values to be used for the h and k-parameters of various heteroatoms. Part of the problem is that there are several variations of MO theory and each will yield somewhat different parameter values with a given application.

We should distinguish, for example, the nitrogen in pyridine from a pyridinium nitrogen. In the former case, the heteroatom contributes two electrons to the π-system; in the latter case it contributes one. In the second part of the analysis of your experimental data, you will use a "canned" HMO computer program to determine the energy levels and molecular orbitals of the π-states of the dye molecules (as a function of β). By comparison of these results with your experimental data, you will determine an empirical value for β. Note that this program incorporates values for the heteroatom parameters h and k. You will need only to specify the location and type (e.g., pyridine-type nitrogen) of each heteroatom in the molecule to be studied.

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4.4: References and Additional Reading

Duke students can find additional reading materials at the link below, many of which are listed in the references below.

Duke students, click here for additional readings, or find the resources below in the Library (yes, the physical library!)

References

1. Castellan, G. W., Physical Chemistry, Addison-Wesley, Reading, Mass., 1972, Chapters 19-22.

2. Barrow, G. Physical Chemistry, 3rd ed., McGraw-Hill, New York, NY, 1973, Chapters 3 and 12.

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5: WHAT CAN FTIR TELL US ABOUT A MOLECULE?

Learning Objectives

- **Develop an energy level diagram and a mathematical model** that explains the pattern of peaks observed in an IR spectrum of gaseous HCl (or other diatomic).
- Use computational methods to **fit a model to experimental data**, and to **evaluate and refine the model.**
- **Explain** the quantum mechanical phenomenon of roto-vibrational coupling.
- I**dentify, describe, and interpret the molecular constants** that can be extracted from gas-phase IR spectra.
- **Describe the impact of instrument resolution settings** on what information can be revealed in an IR spectrum and on the precision of molecular constants derived from the spectral data.

5.1: Pre-lab Assignments

5.2: The Electromagnetic Spectrum and Molecular Transitions

5.3: Experimental and Instructions

5.3.1: Instructions for using the Nicolette iS50 FTIR

5.4: Background on Rotovibrational Spectroscopy

5.4.1: Rotational Transitions Accompany Vibrational Transitions

5.4.2: Transition Intensities

5.4.3: The Pure Rotational Spectrum has Unequal Spacings

5.4.4: Anharmonicity and Vibrational Overtones

5.5: References

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5.1: Pre-lab Assignments

📅 **Due:** Each part of this assignment must be completed before 1:00 PM on each scheduled lab meeting day (see syllabus schedule).

- **Part I is due prior to the first week's Wet Lab meeting (see syllabus agenda).**
- **Part II is due prior to the second week's Wet Lab meeting (see syllabus agenda).**

🕒 **Time:** Plan at least two hours to complete this assignment each week.

🎯 **Purpose**: These pre-meeting assignments are designed to help you arrive to each week's meeting prepared to engage in thoughtful discussion and to conduct the experimental work.

This module has two parts and is usually completed over two laboratory meetings. Each meeting includes **Wet Lab** work, thus you should prepare for both meetings by dressing appropriately for lab and bringing your own safety eyewear. Wear PPE and gloves when handling hazardous materials.

For both meetings, there is a written pre-lab assignment as described below. Complete the **GENERAL PRE-LAB ASSIGNMENT** for both meetings as well as the specific assignment for each meeting. Part I corresponds to the first meeting, and Part II corresponse to the second meeting.

Specific Pre-Lab Assignment for Part I: *What can FTIR tell us about a molecule?*

📅 **Due before Meeting 1**

Read sections 5.1 through 5.3 of this manual and complete the GENERAL PRE-LAB ASSIGNMENT for this part of the module. Then complete the following written assignment and submit your work before the deadline.

1. Consider the types of molecular motions and their energies:
   a. What types of motion can gas-phase molecules exhibit?
   b. In general, what type of motion allows molecules to absorb infrared radiation?

2. The frequency of electromagnetic radiation is often reported in units of wavenumbers (cm^{-1}). Consider the equation $E = \frac{hc}{\lambda}$ and to determine whether wavenumbers (use units as your guide) are directly or inversely proportional to energy.

3. Consider a hypothetical diatomic gas with a typical harmonic frequency of 2000 cm^{-1}.
   a. *Apply the Harmonic Oscillator Model*: Draw the energy level diagram corresponding to the vibrational energy levels for this molecule (assume an ideal harmonic oscillator).
   b. *Energies of Molecular Motion*: To which region of the electromagnetic spectrum do transitions between these energy levels belong?
   c. *Predict a spectrum*: A sample of this diatomic gas is placed in a spectrometer capable of measuring absorbance in the range 1000 – 5000 cm-1. Predict the appearance of the spectrum (intensity of absorbance vs. frequency). Put frequency (in cm^{-1}) on the x-axis and intensity of absorbance on the y-axis. Draw the spectrum and explain you reasoning.
   d. *Link your prediction to the model*: Go back to the energy level diagram you drew in 3A. Add an arrow to your energy level diagram from 3A to represent each transition drawn in your spectrum in 3C.

Specific Pre-Lab Assignment for Part II: *How does the instrument resolution affect the results?*

📅 **Due before Meeting 2**

Review the group discussion guide worksheets that you completed during the first meeting, the data you collected, and your data analysis. Read section 5.4 of this module and complete the GENERAL PRE-LAB ASSIGNMENT for this part of the module, and the items below.

4. Find the rotovibrational models that you derived and fit to the experimental data in the previous meeting. Write the expression for each. Then define each one of the parameters (with units).
5. Describe how you can identify each of the parameters' values from theory or calculate it using the experimental data you collected.
   - m
   - $\tilde{\nu}$
   - α
   - $\tilde{B}$
   - $\tilde{D}$
   - Moment of Inertia (I_e)
   - Equilibrium bond length (r_e)
6. Show the equations by which you would find uncertainty in each parameter using the results of nonlinear fitting ($\Delta\tilde{\nu}$, $\Delta\alpha,;\ \Delta\tilde{B},\ \Delta\tilde{D},;\ \Delta I_e,\ \Delta r_e$).
7. *Predict the effect of resolution*: What will happen to the FTIR spectrum and the derived molecular parameters as instrument resolution is changed from 8 cm^{-1} to 0.5 cm^{-1}? Show your prediction by sketching the spectrum for at least three different resolutions. Describe the trend you expect in the molecular parameters as resolution is varied.

Adapted from Beck, Jordan P., and Diane M. Miller. “Encouraging Student Engagement by Using a POGIL Framework for a Gas-Phase IR Physical Chemistry Laboratory Experiment.” *Journal of Chemical Education* 99, no. 12 (December 13, 2022): 4079–84. https://doi.org/10.1021/acs.jchemed.2c00314.

Additional reading: (available in the library, Duke students click here)

- Part I. Instrumentation, *Journal of Chemical Education,* **1986,** *63* (1), A5. (This is a description of how the Michaelson Interferometer is applied in FTIR spectroscopy. See also the video lined below.)
- Shoemaker, D.P., Garland, C.W., and Nibler, J.W. Experiments in Physical Chemistry, 6th ed., McGraw-Hill, New York, 1996, Chapter XIV, **Experiment 37**.
- McQuarrie, D.A. and Simon, J.D. "Physical Chemistry: A Molecular Approach", University Science Books, CA, 1997, Sections 13.2-13.4, 18.4-18.5); Atkins, P., Physical Chemistry, 5th ed., sections 16.8 – 16.11
- Silbey, R.J., Alberty, R. A. Bawendi, M.G., Physical Chemistry, 4th ed., Sections 13.4, 13.6 and 13.7, for a discussion of rotation-vibration spectroscopy of diatomic molecules.

Optional videos

Dr. Welsher's P-Chem lectures are on YouTube!

In addition, the videos below provide a nice introduction and demonstration of the theory and techniques you will use.

Introduction to the Michaelson Interferometer in FTIR

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

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5.2: The Electromagnetic Spectrum and Molecular Transitions

Electromagnetic radiation, or light, exhibits dual behavior as both waves and particles. Wave properties, such as refraction, best explain phenomena like light passing through different mediums. Conversely, particle behavior provides a more accurate description in certain scenarios, like absorption and emission. The nature of electromagnetic radiation remains unclear, with wave and particle models coexisting since the development of quantum mechanics in the early 20th century. Despite this ambiguity, these dual models effectively characterize electromagnetic radiation.

It consists of oscillating electric and magnetic fields that travel through space at a constant velocity. In a vacuum, the speed of light (c) is $2.99792 \times 10^8 \frac{m}{s}$. When passing through a medium other than a vacuum, its velocity (v) is slightly less than c, with the difference being <0.1%. For practical purposes, the speed of light is often approximated as $3.00 \times 10^8 \frac{m}{s}$. The oscillations in the electric and magnetic fields are perpendicular to each other and the wave's propagation direction. A model of plane-polarized electromagnetic radiation, featuring a single oscillating electric field and a single oscillating magnetic field, is illustrated in Figure 5.2.1.

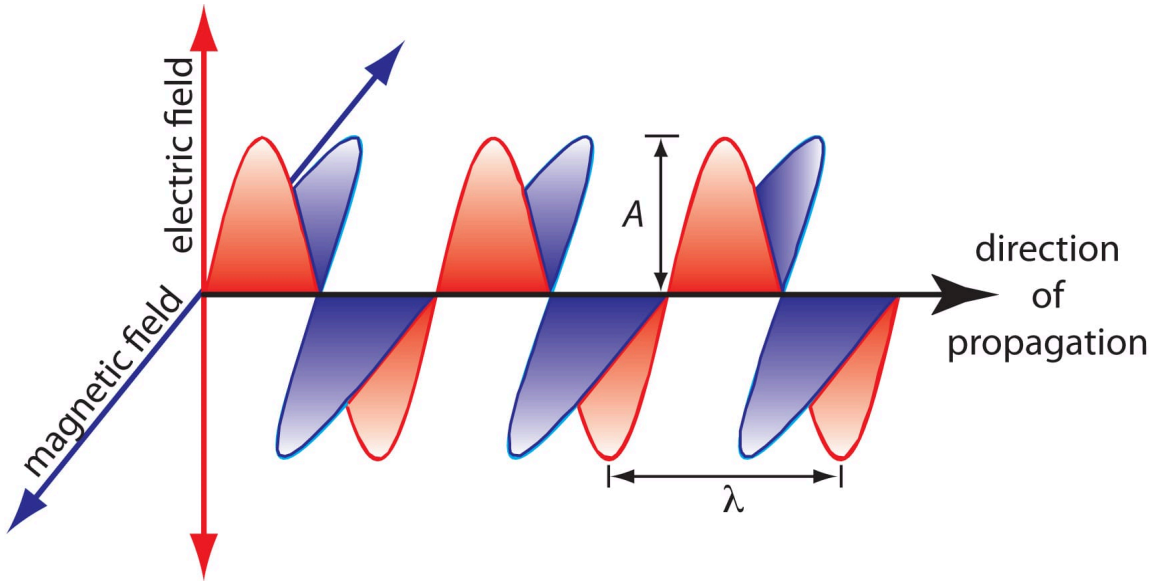


Figure 5.2.1: Plane-polarized electromagnetic radiation showing the oscillating electric field in **red** and the oscillating magnetic field in **blue**. The radiation's amplitude, *A*, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \phi) \tag{5.2.1}$$

where A_t is the magnitude of the electric field at time t, A_t is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at t = 0. The identical equation for the magnetic field is

$$A_t = A_m \sin(2\pi\nu t + \phi) \tag{5.2.2}$$

where A_m is the magnetic field's maximum amplitude.

Units of energy

The **wavelength**, λ, is defined as the distance between successive maxima (Figure 5.2.1). The relationship between wavelength (in m) and frequency (in s^{-1} or Hz) is given below. Wavelength is usually expressed in nanometers (1 nm = 10^{-9} m) for ultraviolet and visible light, and in microns (1 μm = 10^{-6} m) for infrared light.

$$\lambda = \frac{c}{\nu} \tag{5.2.3}$$

Wavelength is a unit used often by chemists, especially in UV-vis spectroscopy. Because it is inversely related to energy (ie smaller wavelengths are higher energy), many scientists prefer units that are directly proportional to energy. An alternate unit, the **wavenumber**, $\tilde{\nu}$, is used frequently, especially in infrared spectroscopy. In general it seems to be the preferred unit of physicist due to its direct correlation to energy. It is useful to know how to convert between these two commonly-used units. The unit $\tilde{\nu}$ is simply the reciprocal of wavelength.

$$\tilde{\nu} = \frac{1}{\lambda} \tag{5.2.4}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Keeping symbols straight

Heads up! The word "frequency" refers to cycles per unit time, but can also be measured in a length scale. Frequency measured in cycles per seconds (s^{-1} can be expressed in the metric base unit Hertz, and can have the symbol f or ν. When it is expressed in a length scale, like wavenumbers (cm^{-1}), it has the symbol $\tilde{\nu}$.

- When converting units from ν (in s^{-1}) to λ, use the speed of light to convert between time and length scales as in 5.2.3.
- When converting from $\tilde{\nu}$ to λ, use 5.2.4 and convert metric units as necessary.

Regions of the Spectrum and Types of Transitions

Electromagnetic radiation spans a wide range of frequencies and wavelengths, prompting the division of this spectrum into distinct regions for convenience, known as the **electromagnetic spectrum** (Figure 2). These divisions are based on the atomic or molecular transitions responsible for the absorption or emission of photons. It's important to note that the boundaries between these regions are not fixed, allowing for potential overlap between different spectral regions.

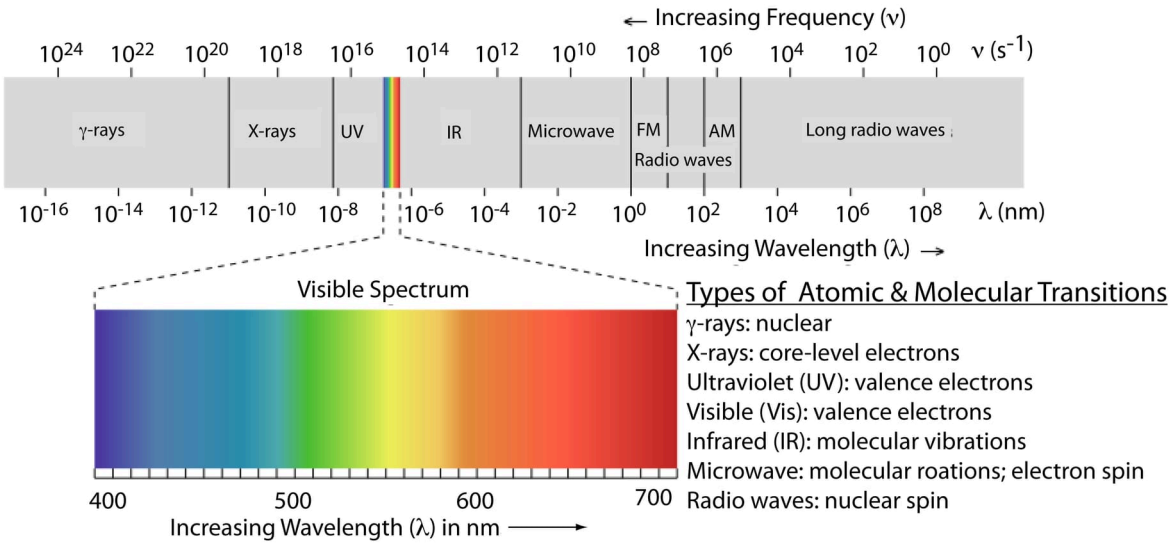


Figure 5.2.2: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

Given the energy levels of molecules and their corresponding wavelengths, we can determine the frequency within the electromagnetic spectrum regions using the equation:

$$\Delta E = E_u - E_l = h$$

Here, h represents the energy change between the upper (u) and lower (l) states.

The frequencies of molecular transitions fall within specific ranges. These ranges are listed in the table below in order of increasing energies.

Table 5.2.1: Each type of molecular motion and its corresponding region of the electromagnetic spectrum. Ranges are approximate.

Region	Wavelengths (nm)	Frequency (cm^{-1})	Frequency (s^{-1})	Transitions
Microwave	~10^9 - 10^6	~ 0.01 - 10	~10^8 - 10^{11}	**rotational transitions**
Infrared	~10^4 - 10^3	~200 - 4,000	~10^{12} - 10^{14}	**vibrational transitions**
Visible and Ultraviolet	~750 - 10	~ 13,300 - 1,000,000	~10^{14} - 10^{16}	**valence electronic transitions**

Contributors and Attributions

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5.3: EXPERIMENTAL AND INSTRUCTIONS

Materials

- **Equipment:**
  - Nicolette iS50 FT-IR Spectrometer
  - Long Path Length Gas Cell with windows that are transparent to IR radiation (KBr windows)
- **Reagents:**
  - Hydrogen Chloride 99+%: Aldrich Chemical Company; Cat # 29,542-6; Cas # [7647-01-0]; FW = 36.46; safety information can be obtained from: Sigma Aldrich (Click).

HAZARD: This experiment uses concentrated HCl (strong acid)!

The concentrated acid used in this experiment is a hazard. Go to the linked Safety Data Sheet and read the safety information related to these compounds:

- Hydrogen chloride is **colorless, pungent, and corrosive** .
- Contact will cause **burns to the skin, severe burns to the eyes, and burns to the respiratory system if inhaled.**
- **Use gloves, protective eyewear, and avoid inhalation** throughout this experiment.

USE CARE: Gas Cells are FRAGILE and the KBr Windows are FRAGILE andare destroyed by water!

The cell is constructed of a glass body with KBr windows at each end. Ensure that the salt windows are kept free of moisture at all times. Please do not touch these windows.When not in use the IR gas cell must be stored in the desiccator.

The Group Notebook (ELN) Template is available through Google Classroom. This template is provided as a guide so that you know what data and information should be kept in a notebook. You may keep your personal notebook in any way you'd like, but you should translate your notes into this template for the group submission.

Part I: What can an FTIR Spectrum tell us about a diatomic gas molecule?

A: Computational prediction of vibrational frequency and bond length

1. Use a computational chemistry program to determine the computationally-predicted **vibrational frequency** and **bond length** of hydrochloric acid gas.
   a. **Perform Equilibrium Geometry Calculation:** Specifically, use density functional theory (DFT) to calculate the equilibrium geometry of HCl gas, determine its vibrational frequency (or frequencies), and the equilibrium bond length (internuclear distance).
   b. **Record Computational Results:** Record the predicted IR spectrum in your group notebook. Also record the predicted frequency of the vibration, the predicted bond length, and any other information you feel is worth recording.

Part IB: Preparation of sample and collection of FTIR spectrum

SEE HAZARD and CAUTION STATEMENTS above.

Use the following method (see video) of preparing a gas cell. Start with the cell filled only with the gases from atmosphere: collect **a spectrum of the background**. Then, add one drop of HCl, allow it to evaporate in the sealed cell, and use the cell to collect **a spectrum of HCl gas.**

Prepare the cell with background gas

1. Put on clean, dry gloves before handling any components of the gas cell.
   Avoid touching the Potassium Bromide (KBr) windows with bare hands, and never expose them to water, as they are made of salt and will degrade upon contact with moisture.
2. Gather all required materials, including:
   - One Pyrex gas cell body
   - Two Potassium Bromide (KBr) windows
   - Two blue end caps
   - Four O-rings
   - Two septa
   - pH paper
   - Concentrated hydrochloric acid
   - Glass pipettes
   - Wipes
3. Insert a small piece of pH paper into one of the inlets of the gas cell.
   Fold the pH paper as needed so that it fits easily inside the inlet.
4. Cap the inlet containing the pH paper with a septum.
   The septum does not need to fold down or form a tight seal; it simply needs to securely plug the opening.
5. Prepare the end caps by placing one O-ring into the groove inside each end cap.
   Use your thumb to press the O-ring evenly into the groove.
6. Place one Potassium Bromide window into each end cap.
   If a window has one side that appears etched or foggy, orient that side so it faces inward toward the cell body.
   Keep the windows dry at all times.
7. Place a second O-ring on top of each Potassium Bromide window.
8. Gently screw the body onto the end caps without distrubing the windows and o-rings.
   Do not overtighten. The Potassium Bromide windows are fragile and can crack or crush if excessive force is applied.
   Tighten only until slight resistance is felt.
9. Collect a background spectrum on the sealed gas cell assembly using the FTIR instrument.

Introduce HCl into the cell

10. Carefully introduce hydrochloric acid into the cell.
    Using a glass pipette, add **one drop** of concentrated hydrochloric acid through the inlet.
    Ensure that the liquid does not contact the Potassium Bromide windows.
    If any acid is spilled, clean it immediately and change your gloves before proceeding.
11. Wipe the outside of the inlet to remove any residual acid, then cap the inlet with a septum.
12. Gently move and rotate the cell so that the liquid drop moves away from the Potassium Bromide windows and toward the center of the cell.
    Rotate the cell slowly to spread the liquid around the inner circumference, increasing surface area and promoting evaporation.
13. Monitor the pH paper.
    The cell is ready when the pH paper indicates the presence of acid (e.g., a color change).
14. Collect the FTIR spectrum of gaseous hydrochloric acid.

Disassemble the cell and clean up

15. Disassemble the cell carefully after data collection.
    Remove at least one septum before unscrewing the end caps.
    Unscrew the end caps slowly, ensuring that the acid does not contact the Potassium Bromide windows.

16. Set the end caps aside carefully and keep the windows dry.
17. Remove the pH paper using a clean glass pipette and tap it out of the cell body.
18. Change your gloves before handling the Potassium Bromide windows! Transfer the windows to their designated storage location inside a desiccator.
19. Flush all remaining cell components thoroughly with water and dry them with a towel.
20. Wipe bench spaces that may have acid residue with a wet towel, followed by a dry towel.
21. Dispose of all acid-contaminated waste in the appropriate waste container.

Data Analysis for HCl FTIR spectrum for Part I

After collecting your first spectrum, please email your results to yourself, your group, and your instructors. Then assemble your group and begin group discussion and analysis of the data. The files linked at the top of this page will guide you to analyze the spectrum, derive mathematical models to fit the data, and calculate molecular parameters from the fits. (links copied here for convenience: Shared Files for Duke Students). Your instructors will be on hand to help guide you if you get stuck.

Part II: How does instrument resolution effect the certainty of derived parameters?

In Part II, you will collect the spectrum of HCl gas at different instrument resolutions to determine how instrument resolution affects what the IR spectrum can show us, and how instrument resolution affects the uncertainty in the results.

If you finish with part I early, you may be able to collect Part II data in the first lab period. Otherwise, data collection for Part II will happen in the second week of this module.

5.3.1: Instructions for using the Nicolette iS50 FTIR

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5.3.1: Instructions for using the Nicolette iS50 FTIR

You will use a Nicolet iS50 FT-IR Fourier Transform Infrared (FTIR) Spectrometer to collect FTIR spectra. Below are instructions for its use.

Note on Collecting Data

This is a single-beam instrument: there are two steps for collecting any sample spectrum.

1. **Record a background interferogram of the gas cell containing only air.**
   A fast Fourier transform (FFT) will be applied to obtain the background transmittance spectrum.
2. **Introduce your gas sample into the same cell and record a new interferogram.**
   The software will perform FFT analysis on this interferogram to obtain the transmittance spectrum of your sample. To calculate the sample's transmittance spectrum, this spectrum is then ratioed against the single beam background spectrum. The absorbance spectrum of your sample will be calculated by the instrument software, and displayed.

Setup the FTIR Instrument

1. Check the sample holder in the spectrometer to make sure there is nothing blocking the path of the infrared beam.
2. Mount the sealed gas cell on the gas cell holder (it should contain only air).
3. Close the cover and allow the sample compartment to be purged with dry, CO_2-free air for at 2 minutes, noting the time so that the purge time is reasonably accurate. While the chamber is purged, set up the software.
4. The Omnic software may already be loaded. If not, load it by clicking the 

icon on the Windows desktop. As the software loads you will see a blue light turn on at the top front right side of the instrument.

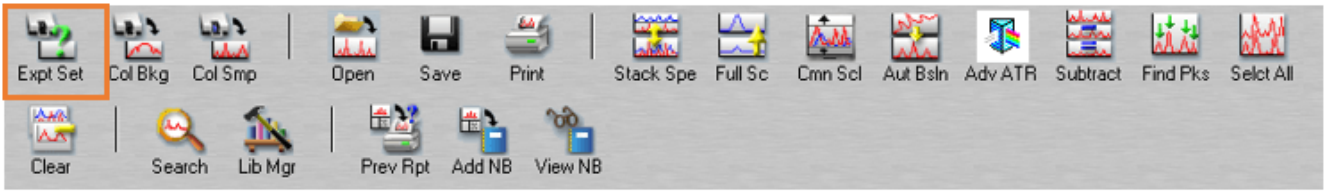


Figure 5.3.1.1: The Omnic Button Bar. (CC-NC-BY-DUKE CHEM)

5. Click the **Experiment Setup** from the toolbar (Figure 5.3.1.1), and go to the **Collect** tab (Figure 5.3.1.2). Enter the appropriate settings. The settings for your first set of scans is below:
   - No of scans: **16 scans**
   - Resolution: **8 cm^{-1}**
   - Final Format: **Absorbance**
   - Experiment Title: **CHEM301L, 8/cm**
   - Experiment Description: Enter whether it is a Background or Sample of HCl

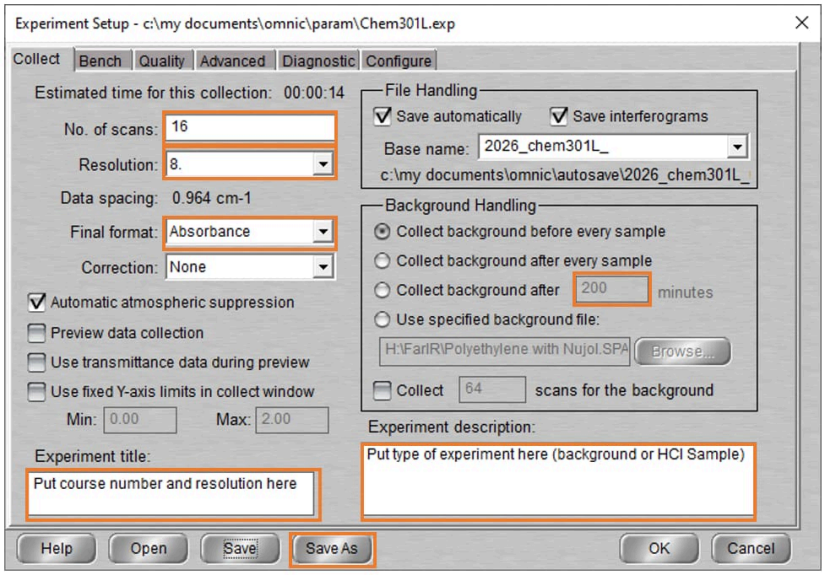


Figure 5.3.1.2: The Collect Pane of the Experiment Setup Window. (CC-NC-BY-DUKE CHEM)

- Click on the **Bench** tab (Figure 5.3.1.3)and wait for the interferogram to appear. The **Max** signal should be around 4 when the cell is in position. Record a screen shot of the Bench tab for your notebook. Click **OK**.

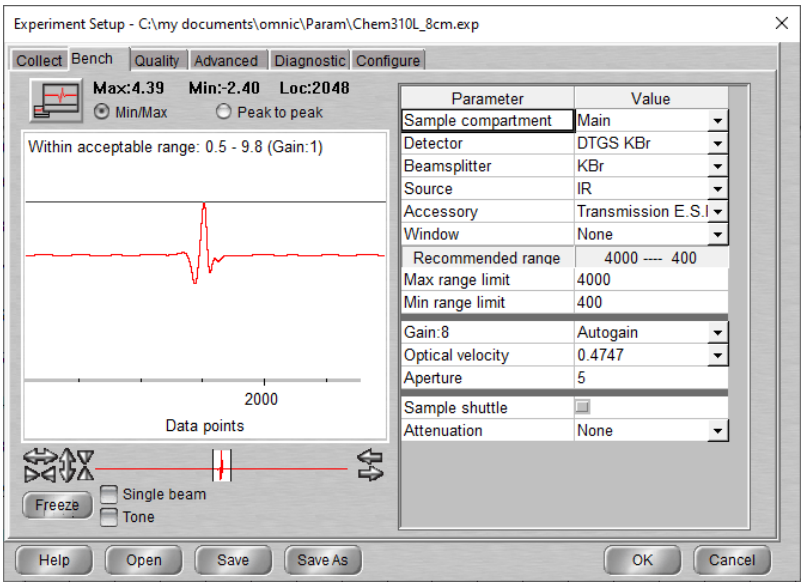


Figure 5.3.1.3: The Bench Pane of the Experiment Setup Window. (CC-NC-BY-DUKE CHEM)

6. Select **Collect Background** from the **Collect** menu (or with the **Col Bkg** button, see Figure 5.3.1.1).
   - Click **OK** when you see the **Confirmation** box. It will take about 4 minutes for the background scan to complete. Part way through, the background scan will be displayed on the main software screen.
   - Once complete, **add the spectrum to the window** when prompted.
   - Note the presence of water vapor, CO_2, and the polymer coating on the in the spectrum (Figure 5.3.1.4). This arises from the atmosphere surrounding the cell (Remember: you gas cell is evacuated at this point).
   - Capture a figure of the background for your ELN using **Edit**→ **Copy** or using the Snipping Tool software.
   - Save your background data file:
   - Go to **File** → **Save as**. Save the file in your course data folder using the file name format **YYYYMMDD_8cm_background_GROUPNAME**.

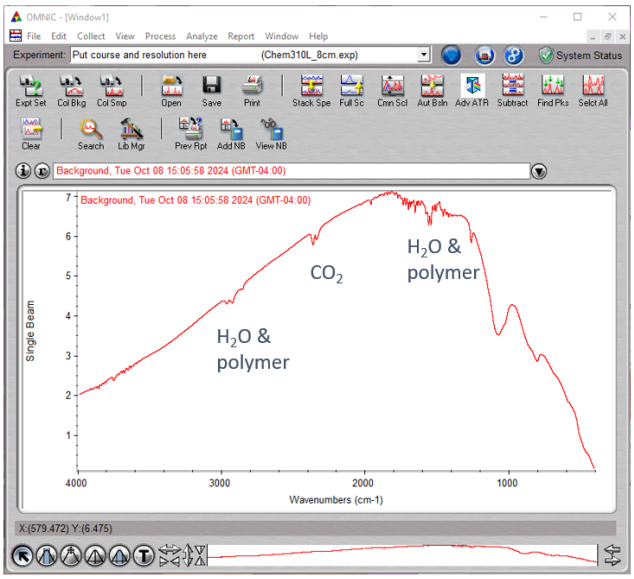


Figure 5.3.1.4: A Typical Background Spectrum collected at 8 cm^{-1} resolution. (CC-NC-BY-DUKE CHEM)

Collect Sample Spectrum

7. Remove the evacuated gas cell from the sample compartment. Under the supervision of your instructors, and following the instructions provided, carefully introduce a gas sample into the cell.
8. Replace the gas cell on the sample holder, and close the door of the sample compartment. Allow the sample compartment to purge for the same time as in the background spectrum. While you wait, do the next step.
9. *If the most recent background spectrum was collected for your cell, then you my skip this step.* Otherwise you must specify which background file should be used for this sample:

   Go to **Experiment Setup** 

and in the *Background Handling* options box, select "**Use specified background file**". Then use the *Browse* button and choose the background file that you collected earlier. Then, press OK when your background file is selected.

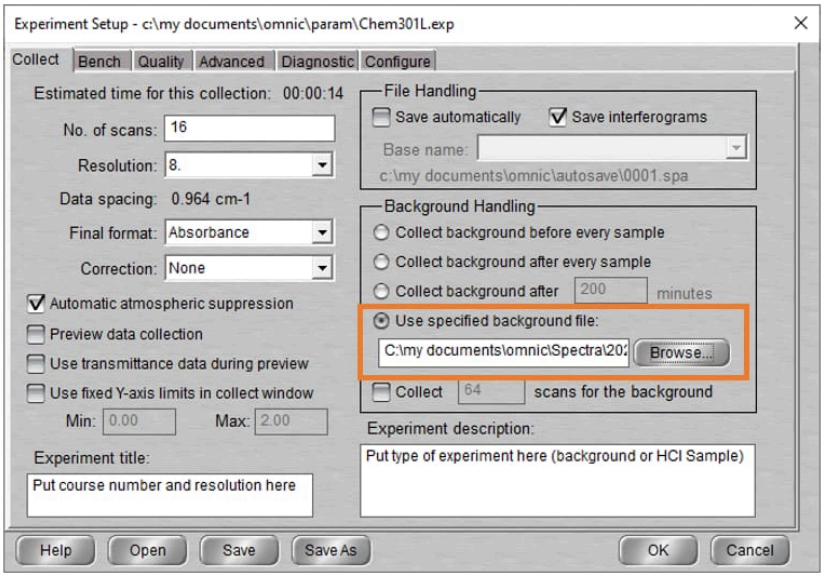


Figure 5.3.1.5: Copy and Paste Caption here. (Copyright; author via source)

10. Select **Collect Sample** from the **Collect** menu (or use the **Col Smp** button). You can enter a title or leave the default date/time when prompted. Click **OK**, and **OK** again in the Confirmation box to start the run.
11. When the scan is complete, add the scan to the window and you will see both sample and background displayed.

12. **Save** the spectrum data file (**File** → **Save as**). Use the data file format **YYYYMMDD_ HCl_8cm_GROUPNAME**
13. **Save the spectrum again** using **Save as** and choose the **.csv file format.** (You need this one for data fitting!)

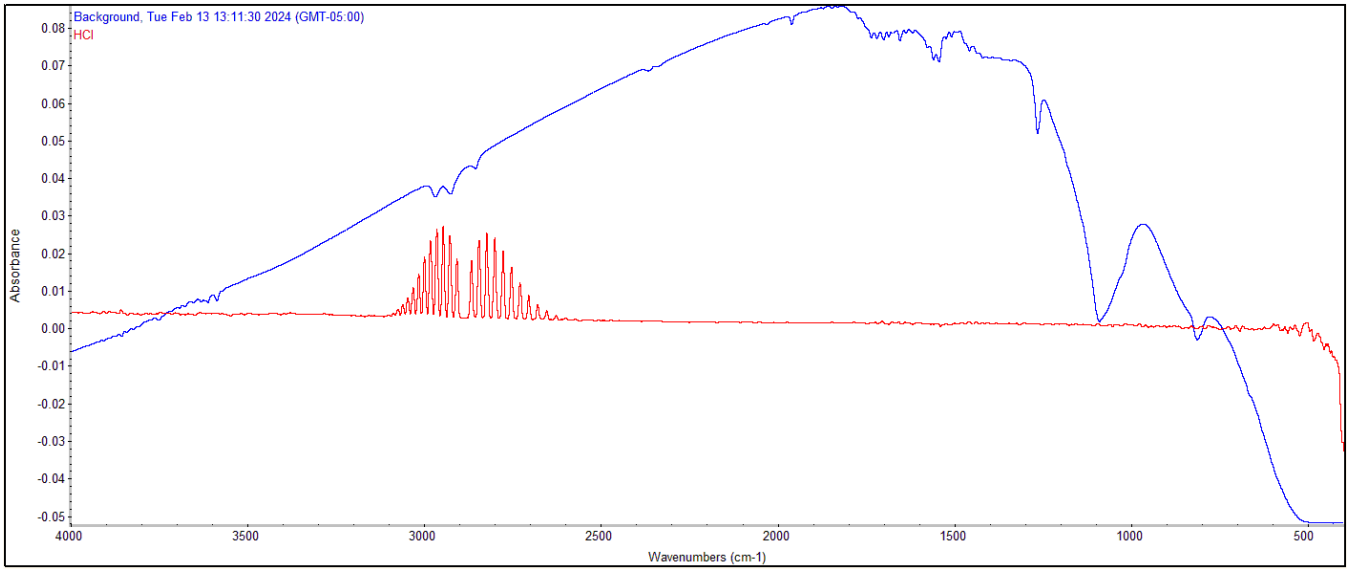


Figure 5.3.1.5: Overlaid Background and FTIR Spectrum at 8 cm $^{-1}$ resolution. (CC-NC-BY-DUKE CHEM)

14. Click on the **background** scan to make it the active scan (red) and select **Hide Spectra** from the **View** menu to remove the background spectrum from view.

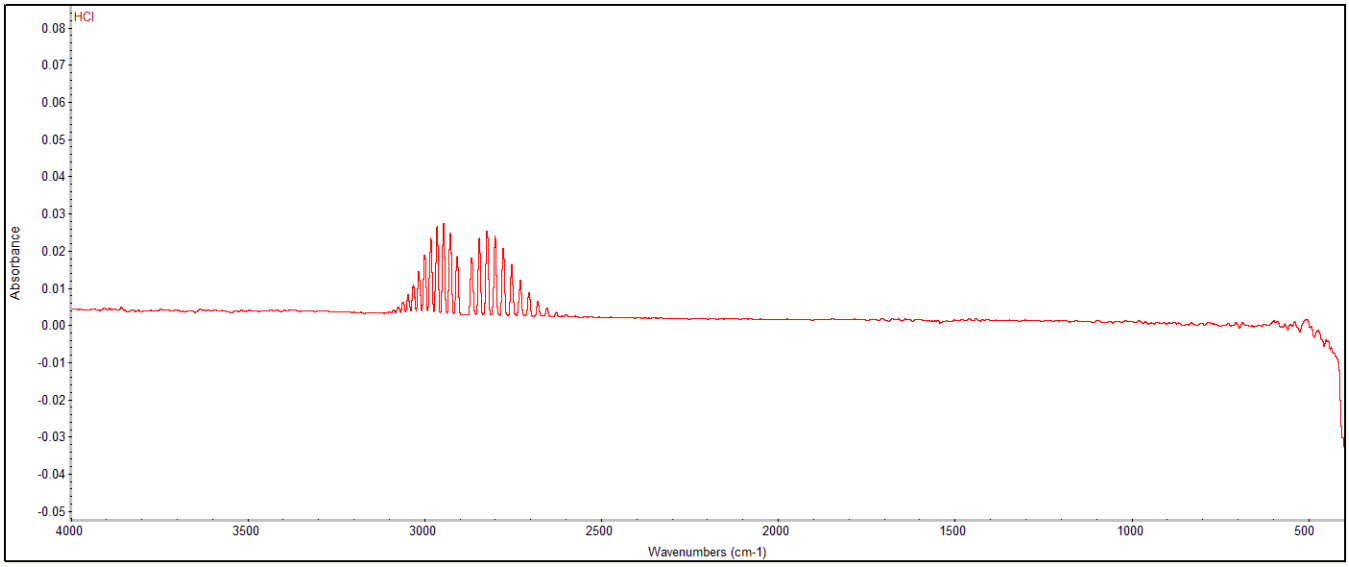


Figure 5.3.1.6: The Sample Spectrum (background is hidden). (CC-NC-BY-DUKE CHEM)

15. Zoom in on the region around the peaks 5.3.1.7. You can do this using the left mouse button to click, drag a box around, and click again to zoom in on a specific region. You can also use the zooming tools at the bottom of the window.

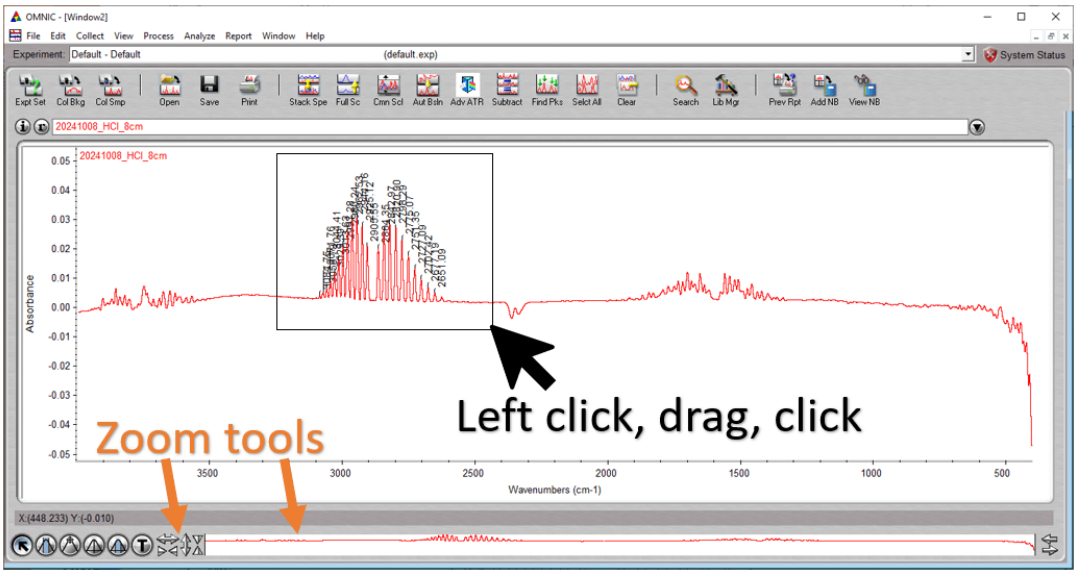


Figure 5.3.1.7: Enlarging the peaks region. (CC-NC-BY-DUKE CHEM)

16. Select **Find Peaks** from the **Analyze** menu or click the 

button (Figure 5.3.1.8. Move the horizontal threshold bar down so that it captures as many of the peaks as possible without getting into the noise at the baseline (see Figure 5.3.1.8 below). You can also adjust the **sensitivity** slider at the left of the screen to fine tune the peak selection. When you have a good selection of peaks, do the following:
    - Capture an enlarged view that contains all of the peaks and peak labels, put this in your ELN.
    - Click the **Clipboard** button to put the peaks table into the Windows Clipboard.
    - Open Excel and paste the clipboard into a spreadsheet (Ctr1 + V).
    - Save the **spreadsheet containing the peaks** in your data folder.
    - Make sure you've saved a screenshot (as already instructed) and that you have saved the excel file containing the list of peaks. Find these files on the computer and open them to be sure you have them and the contain the expected information.
    - Click **Replace** at the top right of the screen to bring you back to the active window.

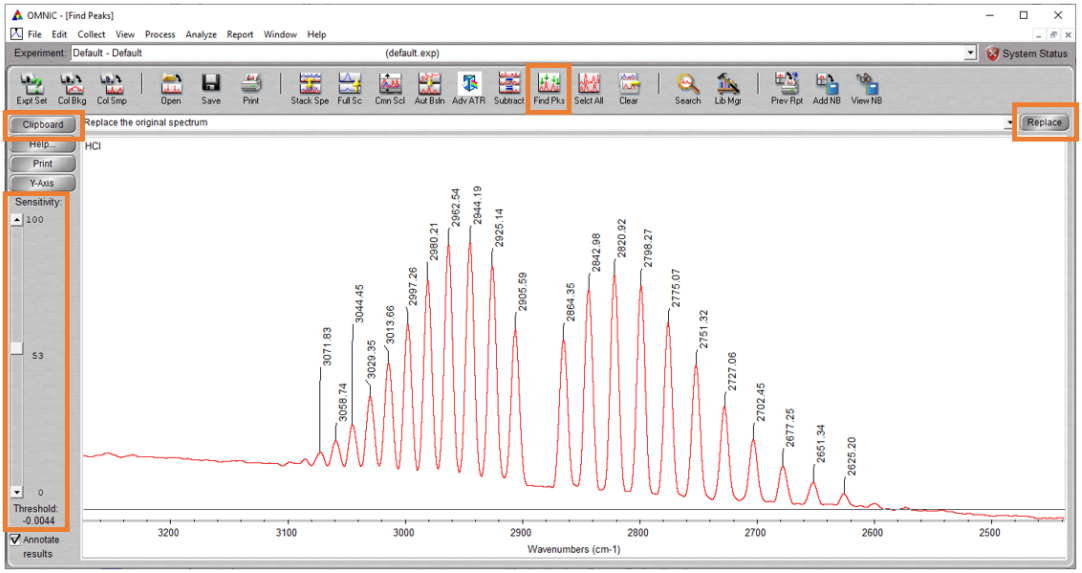


Figure 5.3.1.8: The find peaks result shown in enlarged view for a spectrum taken at 8 cm resolution. Peaks are labeled using the Find Peaks option. A list of found peaks can be copied to the clipboard using the Clipboard button at the top left of the window while "Find Peaks" is active. (CC-NC-BY-DUKE CHEM)

17. If you wish to record the spectrum of a new sample, repeat steps above (repeat background collection if you are collecting

data at a different resolution!).

Remove the gas cell and Shutdown the Instrument

7. Simply **CLOSE THE OMICS SOFTWARE!**
   When you are done with the instrument and all of your work is saved, close the software. You will notice the blue light on the instrument turn off as the instrument goes into standby mode.
8. Remove your sample from the sample compartment and **close the cover**.
9. Follow the instructions for safely cleaning and storing the cell to prevent damage.

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5.4: BACKGROUND ON ROTOVIBRATIONAL SPECTROSCOPY

A note from your instructors

We are working to replace the commercial textbooks used in this course. While we're still working on it, we are providing the following sections (which are still under construction). The section on transition intensities is the only section that was part of the original manual for this course, and is not covered in the Shoemaker textbook.

5.4.1: Rotational Transitions Accompany Vibrational Transitions

5.4.2: Transition Intensities

5.4.3: The Pure Rotational Spectrum has Unequal Spacings

5.4.4: Anharmonicity and Vibrational Overtones

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5.4.1: Rotational Transitions Accompany Vibrational Transitions

The infrared region (IR) of the electromagnetic spectrum is of interest to chemists because it corresponds to the energy of the vibrational modes of molecules (specifically the region between 4000 to 400 cm^{-1}). When the frequency of infrared radiation matches the vibrational frequency of a molecule, the molecule can become vibrationally excited by transitioning from the vibrational ground state to a vibrational excited state. In the case of diatomic molecules, like HCl, there is only one vibrational mode. Thus, we might expect one vibrational absorption band in the IR spectrum.

However, in the gas phase IR spectrum of HCl, there is a complex pattern of bands (see Figure 5.4.1.1). The structure that is observed in the IR spectrum of HCl was one of the early pieces of evidence supporting quantum mechanics and the idea that molecular states (like vibrational and rotational states) are quantized. The person who first measured a high-resolution spectrum like the one shown in Figure 5.4.1.1, and who used this spectrum as experimental confirmation of the Franck–Condon principle, was a **Elmer Imes** (click here for Wikipedia - unfortunately, we couldn't find a public domain photo of him, but google his name and you'll find him!). Imes is best known for his collaboration with James Franck in 1926, where they conducted experiments on molecular spectra (like Figure 5.4.1.1) and provided experimental confirmation of the Franck–Condon principle. This principle relates to the intensity distribution of vibrational transitions in molecular spectra. Imes was the first African American in the 20th century to gain a Ph.D., and he became a physics professor at Fisk University. Elmer Imes's work, along with that of his contemporaries, laid the foundation for our understanding of molecular structures and behaviors, particularly in the realm of rotational-vibrational spectroscopy. His contributions have had a lasting impact on the study of molecular physics and spectroscopy.

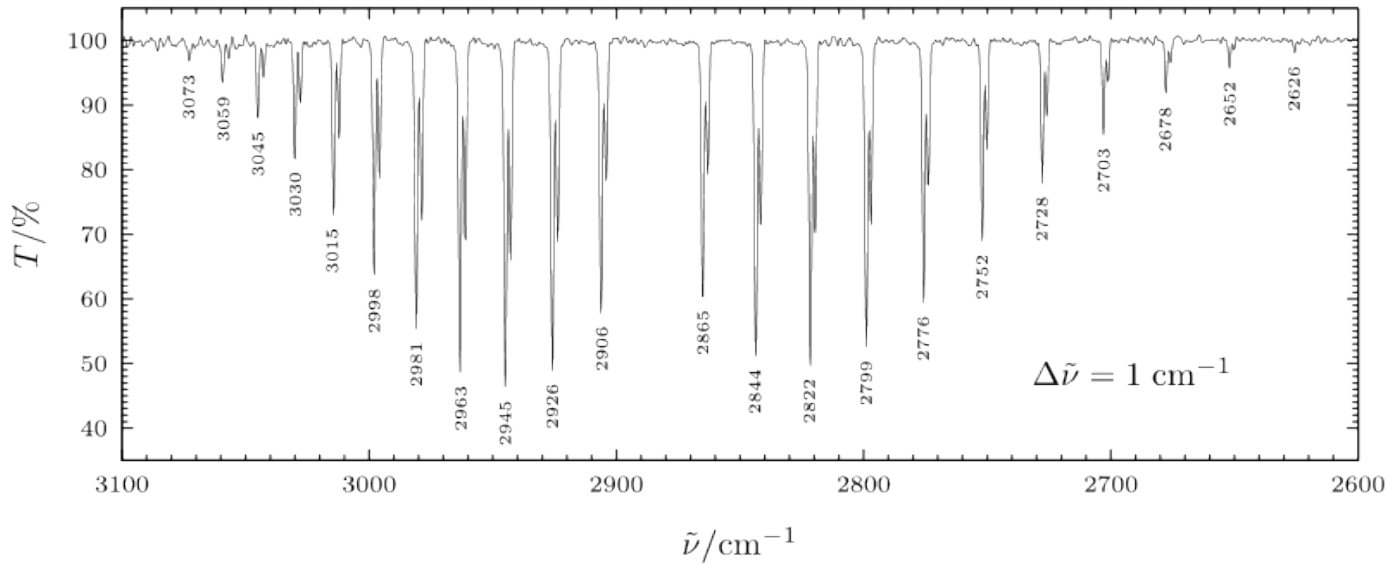


Figure 5.4.1.1. Gas phase FTIR spectrum of HCl. In this view, the data is plotted in a similar fashion as you may have seen in organic chemistry courses. The intensity is shown as % transmission on the Y axis and wavenumbers on the X axis. The X axis is plotted from high to low wavenumber. Figure used with permission from Wikipedia.

While every peak on the spectrum shown in Figure 5.4.1.1 represents a transition from the ground vibrational state to the first vibrational excited state, each represents a unique transition from one rotational state of the ground vibrational state to a different rotational state of the vibrational exited state. This coupling of rotational and vibrational states that appears in the IR spectrum in Figure 5.4.1.1 illustrates the quantized nature of molecular motions.

Models of Molecular Motion

To explain the spectrum shown above, we start by considering all the possible molecular motions and using simple models to describe them.

VIBRATIONAL motions and the HARMONIC OSCILLATOR model

The HCl molecule vibrates along the bond axis. We can treat the molecule's **vibrations** as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete energies given by

$$E(\upsilon) = h\nu\left(\upsilon + \frac{1}{2}\right) \text{ or } \tilde{E}(\upsilon) = \tilde{\nu}\left(\upsilon + \frac{1}{2}\right) \tag{5.4.1.1}$$

Where υ is the vibrational quantum number and can have integer values 0, 1, 2, 3...etc., and ν or $\tilde{\nu}$ is the frequency of the vibration given by:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}} \tag{5.4.1.2}$$

where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{5.4.1.3}$$

At room temperature, nearly 100% of the molecules are in their ground vibrational state $\upsilon = 0$ according to the Boltzman distribution. By convention, the ground vibrational state is indicated by a double prime (") while the exited state is indicated by a single prime (').

- **Ground state:** $\upsilon'' = 0$**, nearly homogeneous population in the ground state at room temp.**
- **First excited state:** $\upsilon' = 1$

At room temperature, the lowest energy vibrational state $\upsilon = 0$ is populated, so $\upsilon'' = 0$. Thus, the only reasonable transition is from $\upsilon'' = 0$ to $\upsilon' = 1$, and $\Delta\upsilon = +1$.

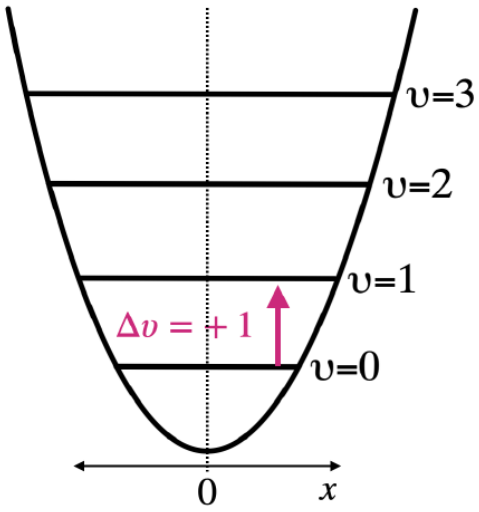


Figure 5.4.1.2: The potential energy (U) well of an 'ideal' harmonic oscillator. The well is defined by the function $U = \frac{1}{2}kx^2$, where k is the force constant and x is the displacement from equilibrium bond length. The vibrational quantum numbers (υ) are indicated for the first three vibrational energy levels. The transition between $\upsilon = 0$ to $\upsilon = 1$ is indicated by the magenta arrow. (Kathryn Haas; CC-BY-SA)

The harmonic oscillation is a useful approximation of a molecular vibration, but has key limitations:

- Due to equal spacing of the energy levels, all transitions would occur at the **same** frequency (i.e. you'd get a single line spectrum). However experimentally many lines are often observed (called overtones).
- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

"Real" bond vibrations are anharmonic

The vibrational energy levels of a real molecule are not evenly spaced and are more like that shown in the illustration in Figure 5.4.1.3, where the energies are more closely spaced as υ increases. However, the harmonic oscillator is a reasonable approximation at $\upsilon = 0$ and $\upsilon = 1$.

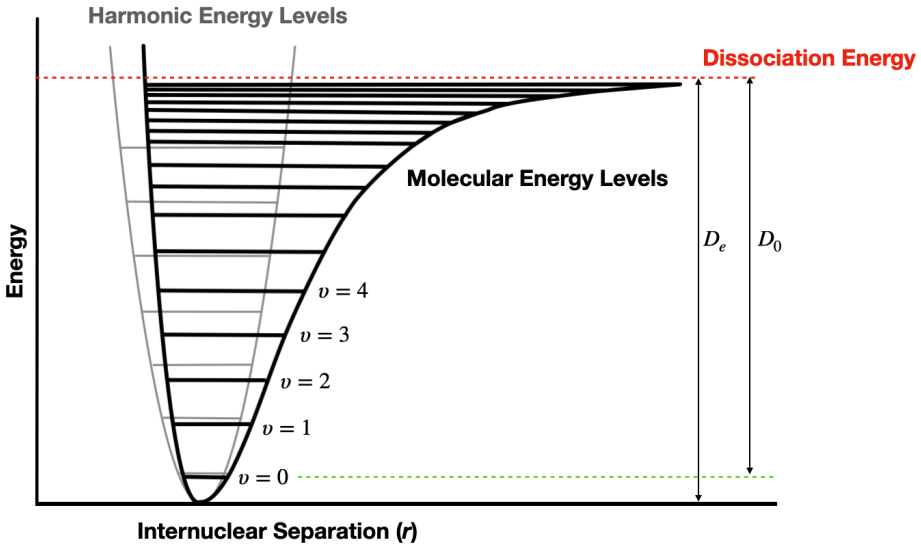


Figure 5.4.1.3: Illustration of vibrational energy levels predicted by the harmonic oscillator model and those of a real diatomic molecule. (Kathryn Haas; CC-BY-SA)

ROTATIONAL motions and the the RIGID ROTOR model

The HCl molecule also has rotational motions. We treat the molecule's **rotations** as those of a rigid rotor (ignoring centrifugal distortion from non-rigid rotor aspects). The energy of a rotation is also quantized in discrete levels given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \tag{5.4.1.4}$$

In which J is the rotational quantum number with integer values 0, 1, 2, 3...etc., and I is the moment of inertia, given by

$$I = \mu r^2 \tag{5.4.1.5}$$

where μ is the reduced mass (Equation 5.4.1.3) and r is the equilibrium bond length.

Experimentally, frequencies of light are measured (in units of cm^{-1}), so it is convinient to use these units in our expressions. The frequency can be divided by hc to give energy in units of wavenumbers. The expression for the rotational energy levels expressed in wavenumbers is $\tilde{E}_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 cI} J(J+1) = \tilde{B}J(J+1)$. And, we can simplify the expression by defining the rotational constant $\tilde{B}$ as

$$\tilde{B} = \frac{h}{8\pi^2 Ic} \tag{5.4.1.6}$$

This gives the allowed energies of rotation, in wavenumbers, as

$$\tilde{E}_J = \tilde{B}J(J+1) \tag{5.4.1.7}$$

Tip: It is important to note in which units you are working. The frequencies and rotational constants can have different units (eg Hz or wavenumbers). To keep track, we are using the tilde $\tilde{X}$ to indicate wavenumber units, but some texts don't do this - they always represent the rotational constant as B, whether in frequency or wavenumbers. Just be sure you are paying attention and are using consistent units in your calcaulations.

Just as in the notations for vibrational states, the convention for notating rotational ground state is by a double prime (") while the exited state is indicated by a single prime ('). The lowest-energy rotational state is $J'' = 0$. Rotational energy levels are very close in energy (much closer than vibrational energy levels), and so at temperatures close to room temperature, there is enough energy so that higher-energy states are populated (e.g. $J'' = 1, 2, 3...$ are also populated). The statistical probability of each rotational state being populated can be calculated using the Boltzmann distribution.

- **Ground state: J''; at room temperature there is heterogeneous population of the rotational states.**
- **Excited state: J'; upon excitation we can also expect a heterogenous population of excited states.**

The rotational energy states are closer in energy than vibrational energy states. And, real molecules undergo rotationas and vibrations simultaneously. Thus, one way to show the rotational energy levels is to superimpose them on a diagram of the harmonic oscillator vibrational energy levels, as is illustrated in Figure 5.4.1.3.

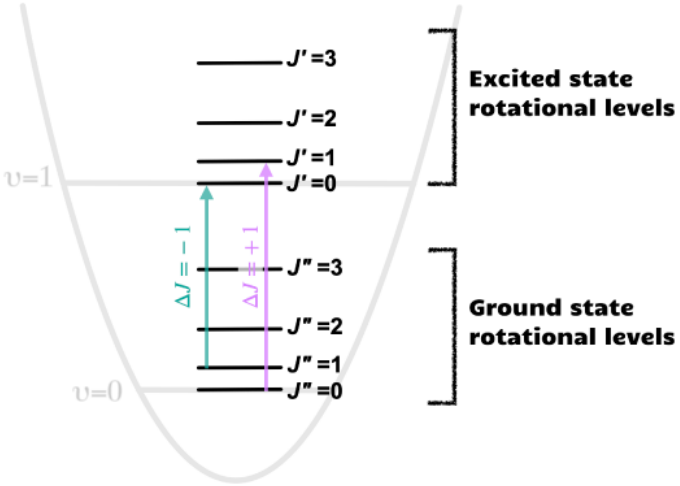


Figure 5.4.1.3: The rotational states are shown superimposed in the vibrational states. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels. All ground state rotational states are indicated by J'' in purple, and rotational states of the excited state are indicated by J' in orange. A transition with $\Delta J = +1$ is indicated by the arrow on the left. A transition with $\Delta J = -1$ is indicated by the arrow on the right. (Kathryn Haas; CC-BY-SA)

Combining rotational and vibrational models

Real molecules are rotating and vibrating simultaneously, and the rotational and vibrational states are coupled. We could express the energies of these motions (in wavenumbers) as a simple combination of rotational and vibrational motions:

$$\tilde{E}_{v,J} = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}_v J(J+1) \tag{5.4.1.8}$$

However, this approximation ignores the fact that the rotational motions affect the centrifugal stretching of a bond, and thus the bond length and vibrational motions are afected by rotational motion. Vice versa, a vibrational excitation would increase the equilibrium bond length (r_e), and would affect the Moment of Inertia (I). A more complete representation of the energies of roto-vibrational states is expressed as a term value, $T(v, J)$, is given below. $T(v, J)$ in Equation 5.4.1.9 combines factors from rotational (rigid rotor) and vibrational (harmonic oscillator) energies, as well as factors that account for anharmonicity, centrifugal stretching,

and the interactions between rotational and vibrational motions.

$$T(\upsilon, J) = \frac{E(\upsilon, J)}{hc} = \tilde{\nu}_e \left(\upsilon + \frac{1}{2}\right) - \tilde{\nu}_e x_e \left(\upsilon + \frac{1}{2}\right)^2 + B_e J(J+1) - D_e J^2 (J+1)^2 - \alpha_e \left(\upsilon + \frac{1}{2}\right) J(J+1) \tag{5.4.1.9}$$

where c is the speed of light, $\tilde{\nu}$ is the frequency in cm-1, υ is the vibrational quantum number, J is the rotational quantum number, and r_e is the internuclear separation. This expression takes into account the following:

- Anharmonicity with the term $-\tilde{\nu} x_e \left(\upsilon + \frac{1}{2}\right)^2$, where $\tilde{\nu} x$ is the anharmonicity parameter in cm^{-1}.
- Centrifugal stretching with the term $-DJ^2(J+1)^2$, where D is a constant.
- The interaction between rotational and vibrational motions with the term $-\alpha \left(\upsilon + \frac{1}{2}\right) J(J+1)$ where α is the rotovibrational coupling constant that accounts for interactions between rotational and vibrational motions.

We can simply this through approximation of the harmonic oscillator by assuming that the the harmonic oscillator is good enough for the case where the vibrational transitions are occurring almost exclusively between the two lowest-energy vibrational states: $\upsilon'' = 0$ and $\upsilon' = 1$. This gives a reasonable approximation that we can use as a model for rotational and vibrational motions of a diatomic:

Approximate allowed energies of roto-vibrational states:

$$\tilde{E}_{\upsilon,J} = \tilde{\nu} \left(\upsilon + \frac{1}{2}\right) + \tilde{B} J(J+1) - \tilde{D}[J(J+1)]^2 - \tilde{\alpha} \left(\upsilon + \frac{1}{2}\right) J(J+1) \tag{5.4.1.10}$$

- $\tilde{E}$ is the energy
- $\tilde{\nu}$ is the vibrational frequency in cm^{-1}
- υ is the vibrational quantum number
- J is the rotational quantum number
- $\tilde{B}$ is the rotational constant
- $\tilde{D}$ is a constant related to centrifugal stretching
- $\tilde{\alpha}$ is the rotovibrational coupling constant in cm^{-1}

Selection Rules for vibrational and rotational transitions on diatomic molecules

- **Vibrational Transition Selection Rules**: The vibrational quantum number can change by 1: $\Delta\upsilon = \pm 1$. However, normally we can assume energy can only go upwards because of the nearly homogeneous population of $\upsilon'' = 0$ near room temperature.
- **Rotational Transition Selection Rules**: The rotational quantum number can change by 1: $\Delta J = \pm 1$. Since at room temperature, $J'' = 0, 1, 2...$ (several different rotational states are populated), transitions to higher and lower-energy rotational states are possible.

The P, Q, and R Branches

These selection rules mean that transitions with ΔJ or $\Delta\upsilon$ equal to 0, 2, 3...etc are not allowed. The fact that the transition $\Delta J = 0$ is forbidden means that a purely vibrational excitation (with no accompanying rotational transition) is not observed in the case of diatomic molecules. The rotational selection rule gives rise to distinct "branches" of the gas phase IR spectrum for diatomics like HCl; They are named using letters P, Q, R in order of increasing energy and corresponding to $\Delta J = -1, 0, +1$, respectively. Due to the unequal spacing of rotational energy levels, each transition requires a different energy.

At the highest energies are the transitions of the R-branch (when $\Delta J = +1$) and at the lowest energies are the transitions of the P-branch ($\Delta J = -1$). Between the P and R branches is the Q branch ($\Delta J = 0$). The Q branch is absent in the gas phase IR spectrum of HCl because $\Delta J = 0$ is forbidden; thus it appears as a gap in the spectrum . Figure $5.4.1.4$ illustrates allowed transitions on the energy diagram .

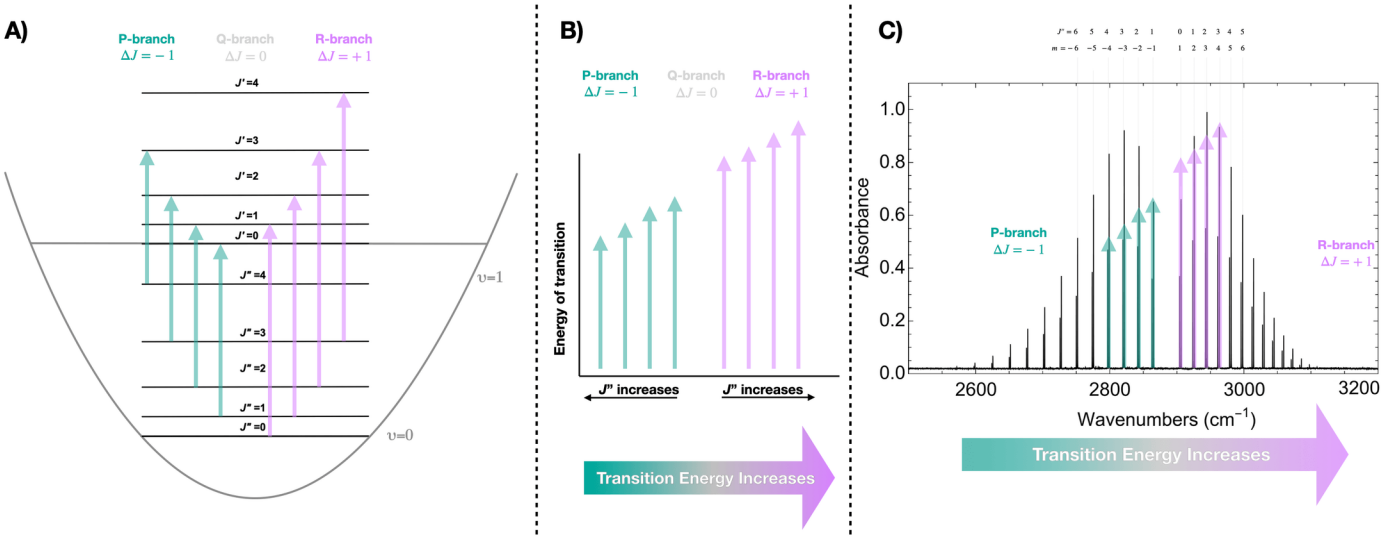


Figure 5.4.1.4: Allowed Rotation-Vibration Transitions are indicated using vertical arrows. The vibrational energy states are indicated with $upsilon$ and rotational energy levels indicated by J. **A)** The rotational energy levels (J) are superimposed on the vibrational energy levels of the ground state ($\upsilon\,''$) and first vibrational excited state (υ'). **B)** Illustration of the relative energy for transitions of P and R branches. Because of unequal spacing between the rotational energy levels, the individual transitions differ in energy. In **panel A**, arrows increase in magnitude from left to right. To illustrate this, each arrow from **panel A** is placed with tails aligned in **panel B** so their relative magnitudes are obvious. The magnitude of the energy transition is qualitatively indicated by the length of the arrow. C) The P and R branches, the m values, and the arrows from Panels A and B are annotated on the FTIR spectrum of HCl (taken at 0.1 cm^{-1} resolution). (Kathryn Haas; CC-BY-SA)

Frequencies of P, Q, and R Branches

The frequency of a rotovibrational transition is the difference in energy (in cm^{-1}) of the excited state and ground state: $T(\upsilon', J') - T(\upsilon\,'', J\,'')$. Thus the frequencies of vibrational transition from $v = 0 \rightarrow 1$ can be calculated from the Equation 5.4.1.9. The calculation is simplified by dropping D_e out of the equation, since D_e (the centrifugal distortion constant) is usually very small. Simplified equations for calculations of the frequencies of each peak in the R and P branches are given below.

R Branch frequencies

For peaks of the R-branch, where allowed J values are $J\,'' = 0, 1, 2, ...$ and $J' = 1, 2, 3...$, and $\Delta J = +1$, the vibrational frequency for a given $J\,''$ is:

$$\tilde{\nu}_R = \tilde{\nu}_0 + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)\, J'' - \alpha_e J''^2 \tag{5.4.1.11}$$

Q Branch (the forbidden frequency)

$$\tilde{\nu}_0 = \tilde{\nu_e} - 2\tilde{\nu_e} x_e \tag{5.4.1.12}$$

*this is the forbidden transition (because $\Delta J = 0$ is forbidden). This is the frequency of the forbidden "vibration-only" transition, and it appears as a gap in the spectrum.

P Branch frequencies

For peaks of the P branch, where allowed J values are $J\,'' = 1, 2, 3, ...$ and $J' = 0, 1, 2...$, and $\Delta J = -1$, the vibrational frequency for a given $J\,''$ is:

$$\tilde{\nu}_P = \tilde{\nu}_0 - (2B_e - 2\alpha_e)\, J'' - \alpha_e J''^2 \tag{5.4.1.13}$$

General equation for all frequencies

We can write a more general equation for the frequencies by defining a new value m, where $m = -J''$ for P branch, and $m = J''+1$ for R branch:

$$\tilde{\nu}(m) = \tilde{\nu}_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2 \tag{5.4.1.14}$$

Trends in peak spacing ($\Delta\tilde{v}$)

Consider a scenario where the interactions between vibrational and rotational motions is negligible, and thus α_e is small. In this scenario, the equations above (equations 5.4.1.11 and 5.4.1.13) would yield a linearly relationship between J'' and $\tilde{\nu}$. In this imaginary scenario, we would expect a spectrum with equally-spaced lines in the P and R branches, where the separation between the lines is $2B_e$ (in other words $\Delta\tilde{\nu} = 2B_e$).

However, in a real diatomic like HCl, there is significant interaction between vibrational and rotational motions, and α_e is significant. The result is a non-linear relationship between J' and $\tilde{\nu}$, where the spacing of the R branch decreases as J'' increases (R branch lines become more closely spaced), and the spacing in the P branch becomes larger as J'' increases (P branch lines become are farther apart).

R Branch peaks become more closely spaced

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{5.4.1.15}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value for increasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$ +(smaller and smaller value) as J increase. Because the rotational frequencies keep getting smaller, the spacing between lines in R branch decreases as J increases.

Increasing in Spacing of Lines in the P Branch with Decreasing J

Using the same analysis as above,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{5.4.1.16}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value even for decreasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$ −(smaller and smaller value) as J decreases. Because the rotational frequencies keep getting larger, the spacing between lines in P branch increase as J decreases.

References

1. McQuarrie, Donald A. Quantum Chemistry. New York: University Science Books, 2007.

Contributors and Attributions

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5.4.2: Transition Intensities

Transition Intensities

The relative intensity of the P- and R-branch lines depends on the thermal distribution of rotational states; more specifically, they depend on the population of the J'' states. The intensity of a spectral line depends not only on the transition probability (selection rules) and the frequency ν (energy of radiation), but also on the number of molecules in any initial state. Since most infrared (IR) spectra are observed under conditions of thermal equilibrium, we need only consider the distribution of the molecules over the different quantum states in thermal equilibrium.

According to the Boltzmann equation, the number of molecules dN_E that have a classical vibrational energy between E and $E + dE$ is proportional to $e^{-\frac{E}{k_B T}} dE$, where k_B is Boltzmann's constant and T is the absolute temperature. In quantum theory, only discrete values, $E_{(\nu)}$, are possible for the vibrational energy. The number of molecules in each of the vibrational states is then proportional to the Boltzmann factor $e^{-\frac{E_{(\nu)}}{k_b T}}$. The zero-point energy can be left out, since to add this to the exponent would only result in a multiplication factor that would be the same for all the vibrational levels (including the zero level).

The thermal distribution of the rotational levels (unlike that of the vibrational levels) is not simply given by the Boltzmann factor. We must account for the fact that, according to quantum theory, each state of an atomic system with total angular momentum J consists of 2J+1 energy levels which are degenerate in the absence of an external field; that is, the state has a (2J+1)-fold degeneracy. The number of molecules N_J in the rotational level J of the lowest vibrational state at the temperature T is thus proportional to

$$N_J \propto (2J+1)\, e^{-\frac{F_{(J)} hc}{k_B T}} \tag{5.4.2.1}$$

where $F_{(J)}$ is the rotational term value (equal to $\frac{E_{(J)}}{hc}$). For sufficiently large T or small rotational constant B, the population of the J^{th} rotational level, for N molecules, is given by the following equation [see p. 125 in reference (3)]

$$N_J = N \frac{hcB}{kT} (2J+1)\, e^{-\frac{BJ(J+1)hc}{kT}} \tag{5.4.2.2}$$

Since the factor 2J+1 increases linearly with J, the number of molecules in the different rotational levels goes through a maximum before decreasing with the rotational quantum number. It can be shown[3] that this maximum lies at

$$J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2} \tag{5.4.2.3}$$

This expression clearly shows that J_{max} increases with decreasing B and increasing T. It should be noted that the number of molecules in the lowest rotational level, J = 0, is not zero. With increasing temperature, the band extends over a wider frequency range and the intensity maxima of the two rotational branches move outward and at the same time become flatter.

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase, as seen in Figure 5.4.2.2 .

From this relationship, we can also deduce that in heavier molecules, B will decrease because the moment of inertia will increase, and the decrease in the exponential factor is less pronounced. This results in the population distribution shifting to higher values of J. Similarly, as temperature increases, the population distribution will shift towards higher values of J.

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5.4.3: The Pure Rotational Spectrum has Unequal Spacings

Vibrational energy which is a consequence of the oscillations/ vibrations of the nuclei along inter nuclear axis, is possible only when the distance between the nuclei is not fixed/ rigid; that means the separation between the two nuclei is flexible/ elastic (non-rigid rotator). Consequently, centrifugal force, when the molecule is rotating, tends to fly the reduced mass μ away from the axis of rotation. To keep the mass rotating about the axis, there must be some restoring force to counter balance the centrifugal force. The work done to supply this force is stored as potential energy. Therefore, unlike the case of rigid rotator, total energy of rotation in a molecule comprises of kinetic and the potential energy corresponding to centrifugal force of rotation.

Let r_e is the distance between the nuclei when the separation is taken to be rigid and r_c under the action of the centrifugal force. According to Hook's law, restoring force is proportional to change in internuclear distance $(r_c - r_e)$, or $= k(r_c - r_e)$ which in turn, will be equal to the centrifugal force.

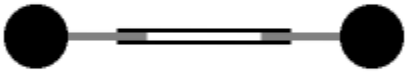


Figure 5.4.3.1: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is stationary. The connection between the weight consists of pistons. When the connecting pistons contract, the rotation rate goes up. When the inward force exerted by the pistons relaxes the weight slide outwards, and the rotation rate goes down. (Public domain; Cleonis).

Centrifugal force,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{5.4.3.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{5.4.3.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{5.4.3.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 5.4.3.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{5.4.3.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{5.4.3.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 5.4.3.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1+\Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{5.4.3.6}$$

$$= \frac{L^2(1-2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{5.4.3.7}$$

using

$$(1+\Delta r/r_e)^{-2} \approx (1-2\Delta r/r_e) \tag{5.4.3.8}$$

$$E_r = \frac{L^2}{2\mu\, {r_e}^2} - \frac{L^4}{k\mu^2\, {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{5.4.3.9}$$

$$= \frac{L^2}{2\mu\, {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2\, {r_e}^6} \tag{5.4.3.10}$$

$$= \frac{\hbar^2\ J(J+1)}{2\mu\, {r_e}^2} - \frac{\hbar^4\ J^2(J+1)^2}{2k\mu^2\, {r_e}^6} \tag{5.4.3.11}$$

Use of Equation 5.4.3.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\ \sqrt{J(J+1)} \tag{5.4.3.12}$$

has been made to obtain relation in Equation 5.4.3.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{5.4.3.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\,\mu\, {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{5.4.3.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\,\mu^2\, {r_e}^6\, c}\ (\text{in cm}^{-1}) \tag{5.4.3.15}$$

First term in the Equation 5.4.3.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 5.4.3.3 wherein k is the spring constant that, as we will see in the following section, plays the same role as in the vibrational motion. In other words, centrifugal stretching constant $\tilde{D}$ is not only measures the influence of centrifugal force, but also hints upon the interaction between the rotational and vibrational motions.

Since $\tilde{D}$ is positive, it is clear from Equation 5.4.3.13 that the energy levels for the non-rigid rotator are slightly lower on energy scale than those of rigid rotator for the corresponding J values; the magnitude of decrease in energy of the non-rigid rotator states increases with J as shown in the Figure 5.4.3.2.

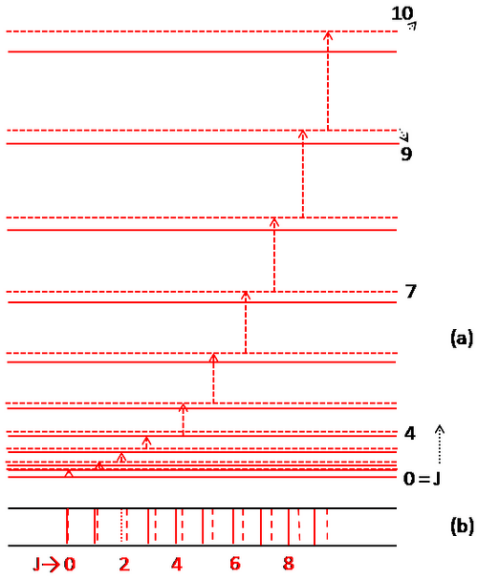


Figure 5.4.3.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

Consequently, on applying the selection rule $\Delta J = \pm 1$, rotational spectrum of a non-rigid rotator consists of a series of lines (red lines) wherein separation, unlike the case of spectral series (broken red lines) of a rigid rotator, between the consecutive rotational lines decreases with increase in J , as shown in the Figure 5.4.3.2. It may be noted that value of D is very small compared to B with the result that the influence of D is significant only for very large J values.

For example, for HCl the values are $B \sim 10.4 \quad cm^{-1}$ and $D \sim 0.0004 \ cm^{-1}$. Usually, D is ignored in the calculations. Figure 5.4.3.2 exaggerates the decrease in energy to visualize its effect. Nevertheless, non-rigid rotator is the model that describes the rotational motion more accurately and hence explains the spectral experimental observations not only in the microwave region but also the rotation-vibration spectra and the rotational structure of the electronic bands discussed in the later sections.

Contributors and Attributions

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5.4.4: Anharmonicity and Vibrational Overtones

Although the harmonic oscillator proves useful for modeling lower energy levels, like $v = 0, 1$, it fails at higher numbers of v. It not only fails to properly model atomic bonds and dissociations, but also is unable to match spectra showing additional lines that are not accounted for in the harmonic oscillator model.

Anharmonicity

Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to a transition of $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure $5.4.4.1$). For example, the parabolic potential of the Harmonic Oscillator approximation means that the vibrations can hold any amount of energy and bonds can stretch to any length, while in real molecules if the atoms are too far apart the bond will dissociate.

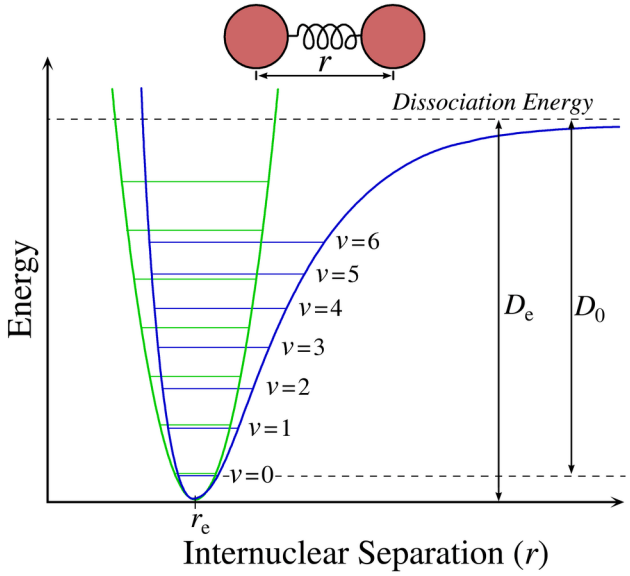


Figure $5.4.4.1$: Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension. (CC BY-SA 3.0; Created by Mark Somoza March 26 2006).

As you can see in Figure $5.4.4.1$, the harmonic oscillator potential well (in green) only roughly fits over the more accurate anharmonic oscillator well (in blue). The blue curve accounts for dissociation at large R values, which the green curve does not even remotely cover. However, this is just one important difference between the harmonic and anharmonic (real) oscillators.

The real potential energy can be expanded in the Taylor series.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \qquad (5.4.4.1)$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

or in terms of a spring constant, ignoring the absolute energy term($V(R_e)$) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2$$

Alternatively, the expansion in Equation 5.4.4.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \tag{5.4.4.2}$$

where

- $V(x_0) = 0$, and $r = R - R_0$.
- k is the harmonic force constant, and
- γ is the first (i.e., cubic) *anharmonic* term

It is important to note that this approximation is only good for R near R_0.

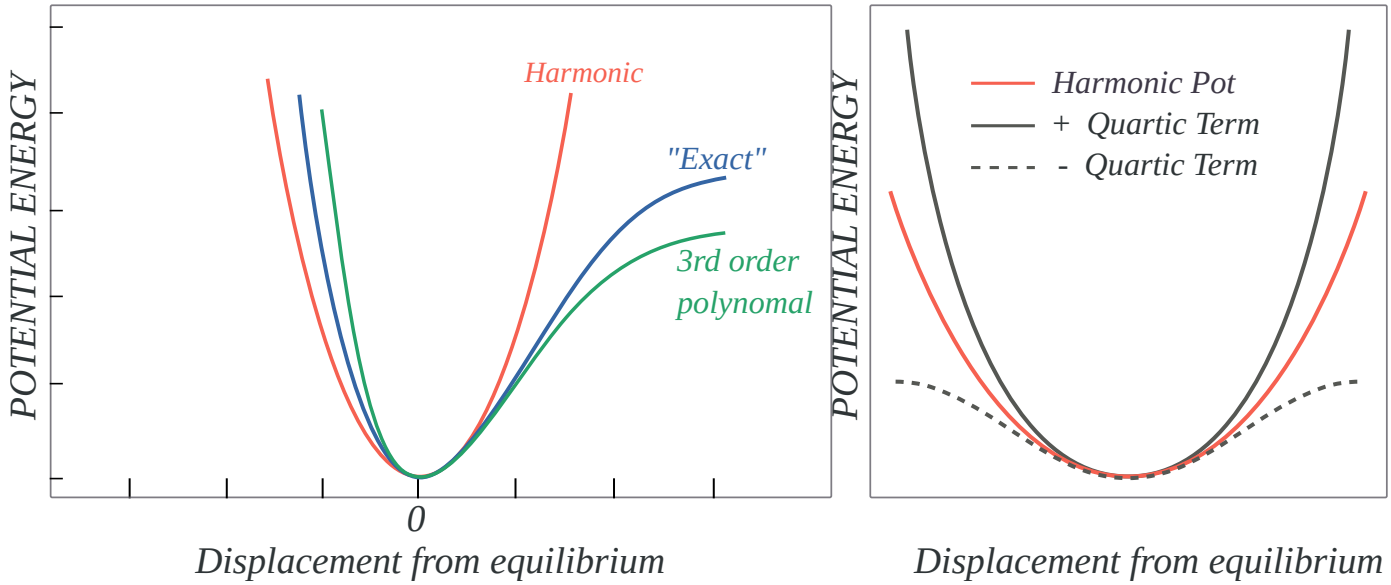


Figure 5.4.4.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

The harmonic oscillator approximation gives by the following energies:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right)$$

When the cubic term in the expansion (Equation 5.4.4.2) is included, and the Schrödinger equation is solved using perturbation theory this gives:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v + \frac{1}{2}\right)^2$$

where $\tilde{\chi_e}$ is the **anharmonicity constant**. It is much smaller than 1, which makes sense because the terms in the Taylor series approach zero. This is why, although E_v technically includes all of the Taylor series, we only concern ourselves with the first and second terms. The rest are so small and barely add to the total and thus can be ignored. To get a more accurate approximation, more terms can be included, but otherwise, can be ignored. Almost all diatomics have experimentally determined $\frac{d^2V}{dx^2}$ for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 have had terms up to $n < 10$ determined of Equation 5.4.4.1.

Overtones

The Harmonic Oscillator approximation predicts that there will be only one line in the spectrum of a diatomic molecule, while experimental data shows there is in fact one dominant line--**the fundamental**--and other weaker lines. How can we account for

these extra lines?

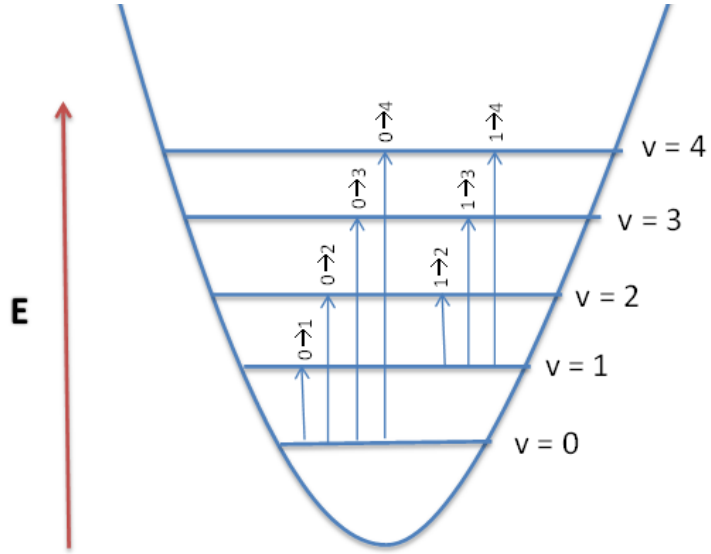


Figure 5.4.4.3 : A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (n > 1) are called hot transitions (hot bands).

Any resonant frequency above the fundamental frequency is referred to as an *overtone*. In the IR spectrum, overtone bands are multiples of the fundamental absorption frequency. As you can recall, the energy levels in the Harmonic Oscillator approximation are evenly spaced apart. Energy is proportional to the frequency absorbed, which in turn is proportional to the wavenumber, the first overtone that appears in the spectrum will be twice the wavenumber of the fundamental. That is, first overtone $v = 0 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

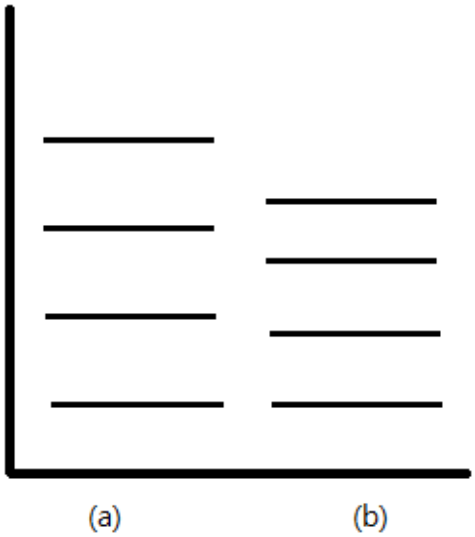


Figure 5.4.4.4 : An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, as implied by Figure 5.4.4.4. Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V = \text{any number}$. That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (the first overtone) or $v = 0$ to $v = 3$ (the second overtone). The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapidly decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be approximately v times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

This is demonstrated with the vibrations of the diatomic HCl in the gas phase:

Table $5.4.4.1$ *: HCl vibrational spectrum.*

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (third overtone)	10 923.1	11 543.6	10,907.4
$0 \rightarrow 5$ (fourth overtone)	13 396.5	14 429.5	13,370

We can see from Table $5.4.4.1$ that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of the transition occuring).

Exercise 13.5.1

HCl has a fundamental band at 2885.9 cm^{-1} and an overtone at 5668.1 cm^{-1} Calculate $\tilde{\nu}$ and $\tilde{\chi}_e$.

Exercise 13.5.2

Write out the Taylor series, and comment on the trend in the increasing terms. Using a test number x, please add terms 3, 4, and 5, then compare this to term 2. How do they compare? We have seen that the anharmonic terms increase the accuracy of our oscillator approximation. Why don't we care so much about terms past the second?

References

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6: MOLECULAR SPECTROSCOPY OF IODINE

6.1: Prelaboratory Assignment

6.2: Introduction

6.3: Potential Energy Curves

6.4: Experimental Part I - Absorption Spectrum of Iodine Vapor

6.5: Experimental Part II - Emission Spectrum of Iodine Vapor

6.6: References and Additional Reading

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6.1: Prelaboratory Assignment

Complete the general pre-lab assignment and submit your assignment on Canvas. In addition, please read the following (Duke Students click here):

Pre-Laboratory Reading

1. McQuarrie and Simon, Chapter 13, sections 13.1, 13.6–13.7; Chapter 15, sections 15.1–15.2, 15.5–15.6
2. Alberty, R.A. and Silbey, R.J. "Physical Chemistry," 2nd ed. (and 4th ed.), Wiley, NY, 1996, Chapter 14, Sections 14.1–14.3, 14.8–14.10

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6.2: Introduction

This module uses a simple homodiatomic molecule, I_2, to demonstrate that molecules have quantized vibrational and electronic states, and that the transitions between electronic and vibrational states can be coupled.

This is a two part module consisting of the following:

I. Collection and analysis of the Absorption Spectrum of Iodine Vapor
II. Collection and analysis of the Emission Spectrum of Iodine Vapor

Chemists use spectroscopy to determine fundamental properties of molecules, and to monitor interesting chemical and physical changes. In this module, you will use linear spectroscopy to monitor the absorption and emission of iodine vapor. This is a demonstration of how scientists use sensitive spectroscopic methods to determine the structure and properties of molecules.

Iodine is purple in color. At room temperature, it is in equilibrium between a solid and gaseous state (see Figure). You can probably draw the Lewis structure and molecular orbital diagram of I_2.

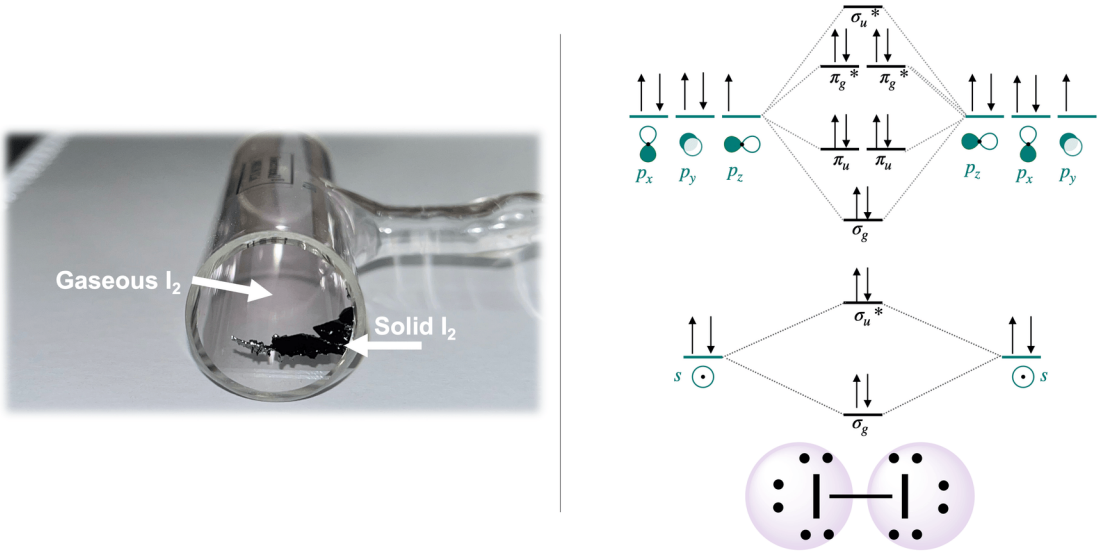


Figure 6.2.1: Left; A spectroscopic cell containing I_2. Right; A Lewis dot structure and an approximate valence molecular orbital diagram for I_2 (CC-BY-NC-SA; Kathryn Haas)

To know what a molecule is at the atomic scale we must use instruments that are more sensitive than our eyes. We know from the Lewis dot structure of I_2 that it consists of two iodine atoms with a single bond between them. But the simple Lewis structure, and rigid dumbbell model that comes to mind, does not describe the dynamics of the iodine molecule.

Consider this for example:

- Using the simple models you learned in Gen. Chem (Lewis dot stuctures or simple MO diagrams), how many electronic transitions should we expect between the HOMO and LUMO of iodine?

You might expect just one electronic absorption from the HOMO to the LUMO. However, the UV-vis absorption spectrum shows many different closely spaced absorptions, and the emission spectrum also shows several wavelengths of light upon excitation.

The fine structure of the electronic absorption and emission spectra are due to the many vibrational states that occur in I_2 when it is in its ground and excited electronic states. In other words, the iodine atoms move in space with respect to each other, which effects the energy of the initial state. Furthermore, the electron excitation alters the bonding in the molecule, effecting vibrational states.

The vibronic structure in a UV-Visible absorption spectrum reveals the vibrational energy levels in the excited electronic states of iodine. From these levels a detailed description of the inter-atomic potential between the iodine atoms in these excited states can be obtained. And, the vibronic structure in the emission spectrum from the excited states of iodine reveals the ground state vibrational levels, from which the ground state potential energy curve can be constructed. Finally, comparison of the ground and excited state potentials determined in this way reveals how the bond length changes and how the vibrational potential softens (or stiffens) on electronic excitation.

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6.3: Potential Energy Curves

Harmonic Oscillator

Within the Born-Oppenheimer approximation, each electronic state in a diatomic molecule has a characteristic nuclear potential surface V(R) describing the interatomic potential energy as a function of interatomic distance R. For a bound diatomic molecule with low vibrational energy this interatomic potential V(R) is similar to that of a harmonic oscillator

$$V(R) = \frac{1}{2}k(R - R_e)^2 \tag{6.3.1}$$

where R-R_e is the deviation of the interatomic separation from the equilibrium value R_e, and k is a force constant describing the strength of the "harmonic spring" that binds the diatomic molecule together.

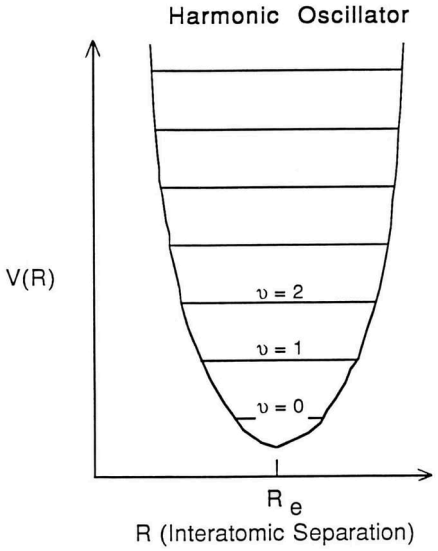


Figure 6.3.1: The potential energy V(R) and vibrational energy levels for a harmonic oscillator. (CC-NC-BY_DUKE CHEM)

The potential energy curve V(R) for a harmonic oscillator is a parabola, and the energy levels are equally spaced, as shown in Figure 5.3.1. The vibrational energy E_υ increases linearly with the vibrational quantum number υ according to the equation

$$E_\upsilon = h\nu\left(\upsilon + \frac{1}{2}\right) \tag{6.3.2}$$

where h is Planck's constant and ν is the vibrational frequency. The vibrational frequency ν is related to the force constant k and the reduced mass μ through the relation

$$\nu = \frac{1}{2\pi}\sqrt{\left(\frac{k}{\mu}\right)} \tag{6.3.3}$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ for a diatomic molecule where m_1 and m_2 are the atomic masses of the atoms.

However, the chemical bonds in real diatomic molecules are not harmonic oscillators.

Anharmonic Oscillator

As a chemical bond stretches it gets weaker, ultimately resulting in dissociation as R approaches ∞. Also, as the bond shortens, interatomic repulsions raise the potential more rapidly than in the harmonic potential. Thus, the potential V(R) for a real diatomic

molecule is anharmonic, and this results in a decrease in the vibrational energy spacings with increasing vibrational energy.

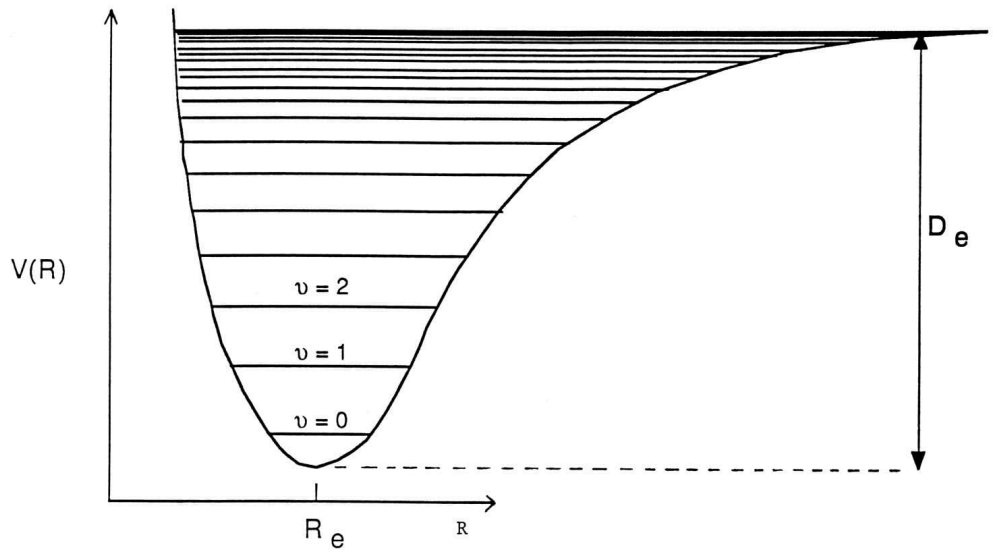


Figure 6.3.2: A typical Morse potential for a diatomic molecule. (CC-NC-BY-DUKE CHEM)

In fact, the difference in energy between neighboring vibrational energy levels approaches zero as the vibrational energy approaches the dissociation energy. Figure 5.3.2 shows schematically a typical anharmonic potential energy surface along with its vibrational energy levels.

Vibrational energies of an anharmonic oscillator

The vibrational energy levels of an anharmonic oscillator can be described by a power series expansion in $\upsilon + \frac{1}{2}$

$$G_\upsilon = \omega_e \left(\upsilon + \frac{1}{2}\right) - \omega_e \chi_e \left(\upsilon + \frac{1}{2}\right)^2 + \ldots \tag{6.3.4}$$

where G_υ is the energy of quantum level υ in cm^{-1}, ω_e is the "harmonic frequency" of the oscillator in cm^{-1}, and χ_e is called the anharmonicity parameter. For the iodine states of interest in this experiment we can truncate the expansion at the second term, as indicated in equation 5.3.4. The difference between successive vibrational energies is then given by

$$\Delta G_{(\upsilon)} = \left|G_{(\upsilon+1)} - G_{(\upsilon)}\right| = \omega_e - 2\omega_e \chi_e \left(\upsilon + 1\right) \tag{6.3.5}$$

By measuring G_υ for a given state, and plotting the change in vibrational energy spacing $\Delta G_{(\upsilon)}$ with respect to $\upsilon + 1$, both ω_e and $\omega_e \chi_e$ can be found. According to equation 5.3.5, this plot should be a straight line with a slope of $-2\omega_e \chi_e$ and an intercept equal to ω_e. (Such a plot is called a Birge-Sponer plot. Hertha Sponer was a well-known and highly respected professor of physics at Duke University, one of only a few women physicists at major research universities during the first half of the twentieth century.)

The Morse Potential

The Morse potential is a simple empirical potential with only two adjustable parameters that incorporates all of these features. In particular it gives rise to the two-term expression for G_υ in equation 5.3.4, with the vibrational energies converging on the dissociation energy D_e (See Figure 5.3.2). The **Morse Potential** has the functional form

$$V\left(R\right) = D_e \left[1 - e^{-a(R-R_e)}\right]^2 \tag{6.3.6}$$

where the Dissociation energy D_e and Morse parameter, a, are related to the parameters ω_e and $\omega_e \chi_e$ by

$$a = \sqrt{\frac{8\pi^2 c\mu\omega_e\chi_e}{h}} \tag{6.3.7}$$

$$D_e = \frac{\omega_e}{4\chi_e}$$

Thus, for this potential, the constants, a, and D_e can be determined from a measurement of ω_e and $\omega_e\chi_e$. While other empirical potential functions provide a better representation of the true shape of the potential for many electronic states of diatomic molecules, for the electronic states of iodine considered here the Morse potential works quite well.

Ground (X) and excited (B) states of iodine

In general, different electronic states have different potentials and different average interatomic separations. For some excited electronic states, the potential may not even have a minimum, or "bound" region. Excitation to one of these "repulsive" potentials would result directly in the dissociation of the molecule, and consequently the absorption spectrum would have no structure. In this experiment, you will focus on electronic transitions between the vibrational levels of two bound electronic states, the ground X $^1\Sigma_g$ state and the excited $B^3\Pi_u$ state. Other electronic states of the iodine molecule will not be discussed here. The potential surfaces for the X and B states can be described by Morse functions. As the molecule dissociates along the ground state X surface, it will separate into two iodine atoms (I + I) in their ground $^2P_{\frac{3}{2}}$ electronic states. However, in the electronically excited B state, dissociation leads to one iodine atom in its ground electronic $^2P_{\frac{3}{2}}$ state, and the other in an excited $^2P_{\frac{1}{2}}$ electronic state (I + I*) (see Figure 5.3.3 below). The energy for the electronic excitation of an iodine atom E(I*) is known quite accurately from atomic spectroscopy, the value being 7603 cm^{-1}. This energy is just the separation in energy between the iodine molecule X and B state potential curves in the limit where R approaches ∞ (See Figure 5.3.3).

Electronic transitions caused by absorption or emission of light will occur between the various ground state vibrational levels (v'') and the excited state vibrational levels (v'). Such transitions involving changes in both vibrational and electronic states are often called vibronic transitions. By convention the various parameters associated with the excited state are designated by $'$ and the parameters for the ground state are designated by $''$, as shown in Figure 5.3.3. The frequency of a vibronic transition (in cm^{-1}) between a ground vibrational state level (v'') and an excited state vibrational level (v') will be given by

$$\nu_{(v'',v')} = \nu_{el} + G_{(v')} - G_{(v'')} \tag{6.3.8}$$

where ν_{el} is the difference in electronic energies of the two potentials at their respective minima, R_e' and R_e'' (see Figure 5.3.3). Note that the energy ν_{el}, the dissociation energies D_e' and R_e'', and the atomic excitation energy of the iodine atom E(I*) are related through the equation

$$D_e'' = \nu_{el} + D_e' - E\,(I^*) \tag{6.3.9}$$

This can be seen in Figure 5.3.3.

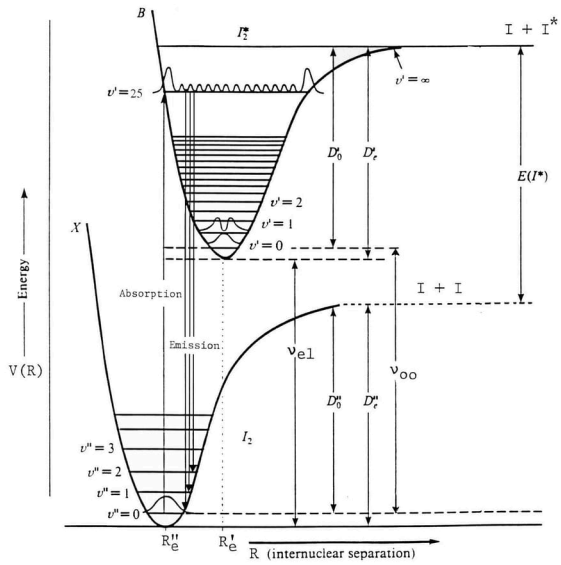


Figure 6.3.3: Schematic representation of the ground (X) and excited (B) states of iodine. Various electronic transitions are indicated by arrows. (CC-NC-BY-DUKE CHEM)

In an absorption experiment, one usually identifies a series of bands (a "progression") that originate from a single ground state vibrational level v'', say $v'' = 0$, and end in a series of different excited state vibrational levels. These bands are then assigned to the appropriate v' quantum numbers (not a trivial task!). If one then calculates the spacing between these bands, it can be seen from equation 5.3.8 that this will yield a linear equation just like equation 5.3.5, but where the independent variable is $(v' + 1)$. From the slope and intercept of this plot the values of ω'_e and χ'_e can be determined, and from these the values of the Morse parameters a' and D'_e for the excited state can be calculated using equations 5.3.7.

In an emission experiment, one usually pumps a single excited state v', and then observes a band progression of transitions back to a number of different ground states v''. These bands can then be assigned, and the separation between them plotted in the form of equation 5.3.5, with $(v' + 1)$ as the independent variable. This allows the ground state parameters ω''_e, χ''_e, a'', and D''_e to be determined.

Consider the molecular potential-energy curves shown in Figure 5.3.3. They relate to different electronic states of the same molecule. Some of the vibrational energy levels of each electronic state are marked, together with some of the vibrational wavefunctions. Before absorption of light occurs, the molecule is most likely to be in the ground vibrational state of the lower electronic state, $v'' = 0$, and so we shall concentrate on that initial level. The form of the lowest vibrational wavefunction shows that the most probable location of the nuclei is near their equilibrium separation R''_e. However, at room temperature the $v'' = 1$ and $v'' = 2$ levels of iodine also have significant thermal populations and so electronic transitions originating from the $v'' = 1$ and $v'' = 2$ levels can also be seen; these are known as **hot bands**.

When an electronic transition occurs, the molecule is excited to the state represented by the upper curve in Figure 5.3.3. According to the Franck-Condon principle, the vibronic transitions occur so fast (on the order of femtoseconds or less) that the nuclear framework remains constant during the actual transition. We may, therefore, imagine the nuclear wavefunction of the molecule as rising up the vertical lines shown in Figure 5.3.3. This is the origin of the term *vertical transition*, which is used to denote an electronic transition that occurs without change of nuclear geometry.

The vertical transition cuts through several vibrational levels of the upper electronic state. The level marked $v' = 25$ is the one in which the nuclei are most probably at the separation R''_e because the wavefunction has maximum amplitude there. Therefore this is the most probable level for the termination of the excitation. It is not, however the only vibrational level at which the transition may end, because several of its neighbors also have a high probability of having nuclei at the separation R''_e. Therefore transitions take place to all vibrational levels in this region, but with greatest probability to the level with the wavefunction that overlaps the initial vibrational state wavefunction most favorably. Transitions from the $v'' = 0$ state of iodine would tend to "miss" upper-level vibrational states with low values of v'. For this reason, these transitions are weak or not observed.

As stated above, the excited state vibrational wavefunctions which have the greatest Franck-Condon overlap with the $v'' = 0$ ground state level, are those with the greatest amplitude near R''_e. For these levels the maximum amplitude in the vibrational wavefunction occurs at the inner "classical turning point" or the edge of the potential well. Such wavefunctions lie at high values

of v' as shown in Figure 5.3.3. Thus we see that the vibrational structure of the spectrum depends on the relative displacement of the two molecular potential energy curves, and a long *progression* of vibrations (a lot of vibrational structure in the spectrum) is stimulated if the two electronic states are significantly displaced.

This Franck-Condon principle can be used to estimate the shift in the potential minimum on excitation, i.e. $R_e'' - R_e'$. The strongest absorption transition (from $v'' = 0$) will be to some particular excited state level $v^{*\prime}$. The separation, $R^{*\prime}$, at the inner turning point of this exited state level can be identified. Assuming the shapes of both the ground and excited state potential curves are known, the two curves can be overlaid so that the minimum in the ground state R_e'' overlaps vertically with the excited state turning point value $R^{*\prime}$. The displacement, $R_e' - R_e''$, can then be read from the plots, or calculated analytically (see references 1 and 4).

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6.4: Experimental Part I - Absorption Spectrum of Iodine Vapor

The ELN template for this entire experiment is available here: ELN for Iodine

Collect the Absorption Spectrum of Iodine Vapor

Here is the Basic procedure for using the Agilent 100 Series UV-Visible spectrophotometer in the Molecular Spectroscopy of Iodine experiment.

There are two sample holders in the instrument. The Sample is placed in the front holder; and, the Reference is placed in the back holder (if applicable).

With both sample and reference holders empty and the cover closed, turn on the instrument with the switch at the front, lower left. Wait two minutes before proceeding further.

Validate the Wavelength Accuracy of the UV-Vis Spectrometer

4.07: UV-vis procedure and instructions for data analysis

Collect the Absorption Spectrum of Iodine Vapor

1. Load the Scan Software by clicking the  icon on the Windows main screen. In a few moments the scan software main screen will appear and will begin to communicate with the instrument. You can follow the progress by monitoring the display at the lower left of the screen. When the traffic light at the top center of the screen turns green, the system is ready. You will see absorbance at the upper left and wavelength at the upper right of the screen.

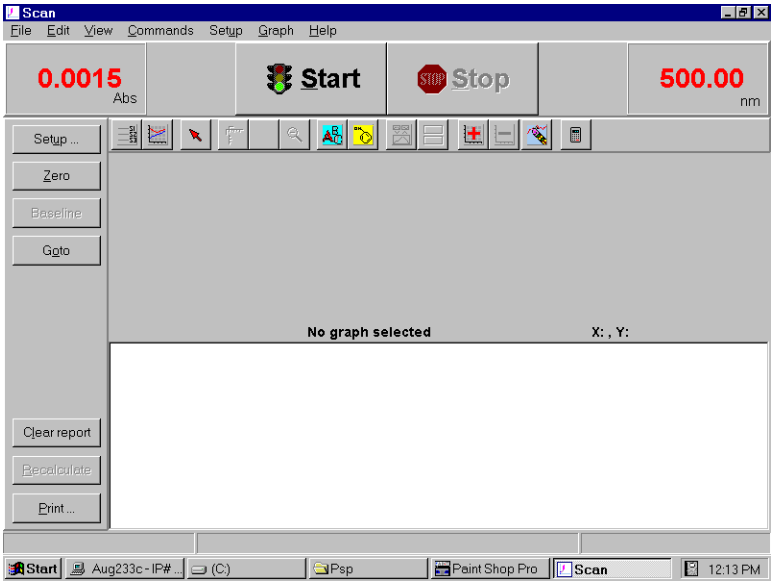


Figure 6.4.4: The Scan Module Main Screen. (CC-NC-BY-DUKE CHEM)

2. Click the  button and wait for the setup screen to appear. Select, first, the Cary tab to begin setting

parameters for your sample runs. Under Xmode, the Mode should be set to nanometers and your scan range from 620 to 490. Under Ymode, the Mode should be set to absorbance and the range from 0.02 to 0.25. The Ave time should be 0.1 seconds and the Data interval should be set to 0.1 nm. This will yield a Scan Rate of 60 nm/min.

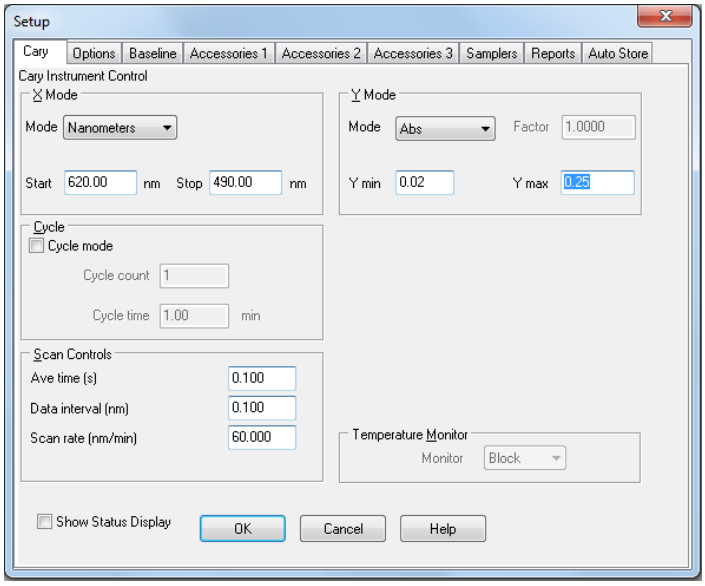


Figure 6.4.5: The Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

3. Select the Options tab on the setup screen and set the Spectral Band Width (SBW) to **0.2 nm**. Select Double Beam Mode. Select UV-Vis as the source and be sure the Source changeover is set to 350 nm. Under Display options you can choose Individual data.

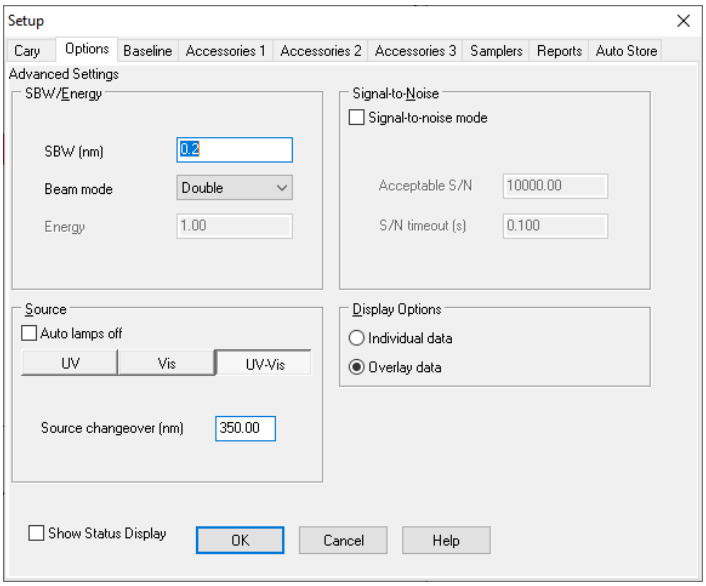


Figure 6.4.6: The Options Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

4. Select the Reports tab. Put your names in the Name box and the title of the experiment in the Comment box. Under Options, check Data Form, Graph, Focused trace. and % Page Height 50. Be sure the Include XY pairs table is not checked. Click Peak Information. Under Peak Table, put a check in All peaks, set the Threshold to 0.0200, and put Peaks in the Peak Type box. Click OK to return to the Setup screen. Choose Select for ASCII (csv). Click OK to return to the main screen.

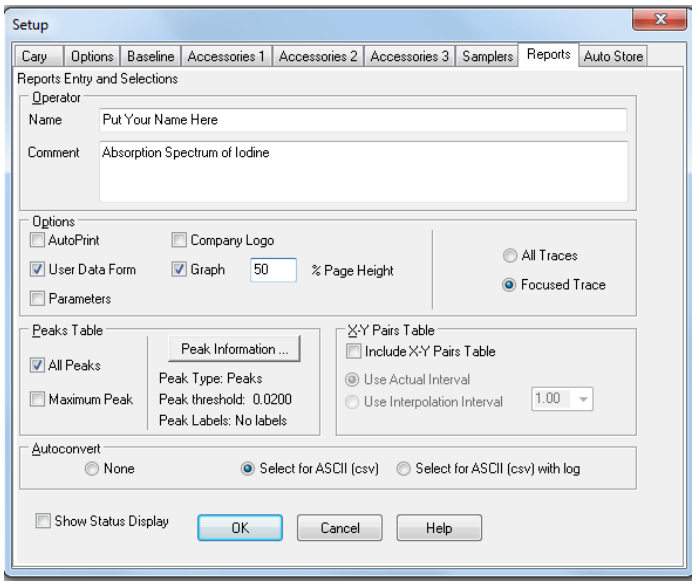


Figure 6.4.7: The Reports Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

5. Remove the 1 cm cuvette holder from the Sample (front) beam of the instrument and replace it with the 10 cm sample cell holder. Place your iodine vapor sample in the Sample holder and close the cover. Click 

to begin your run. You will be prompted for a filename. After naming the file you will be prompted for a sample name. Place the name of the sample (Iodine) in this box. As the run proceeds you will see the spectrum generated in real time on the screen.

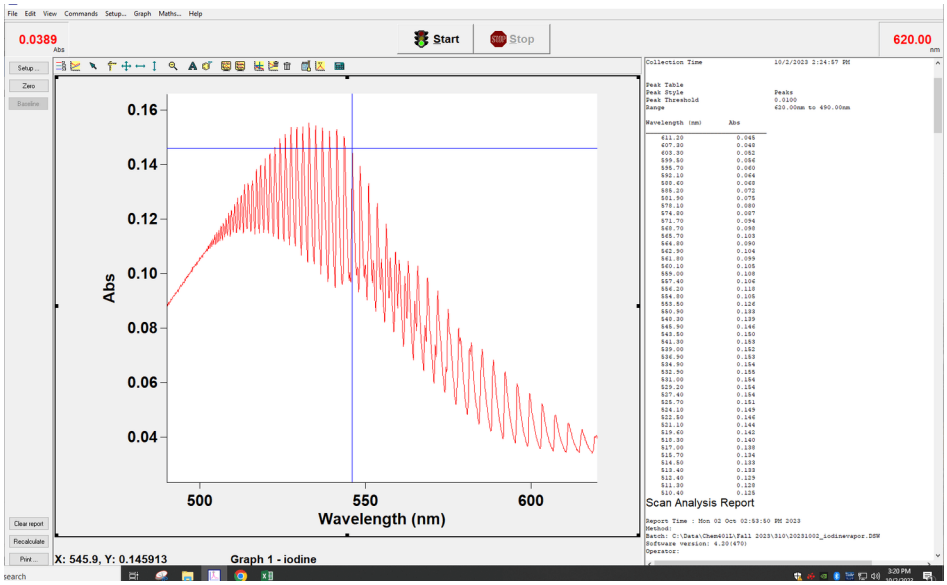


Figure 6.4.8: The Absorption Spectrum of Iodine Vapor. (CC-NC-BY-DUKE CHEM)

6. At the conclusion of the run, find the $v'' = 0 \quad to \quad v' = 25$ transition that is expected to occur at 545.5 nm. Add an annotation to the spectrum to indicate this peak on your spectrum. Also locate the wavelength showing the largest absorption intensity and label it on your spectrum (see note below).

Note

Since the baseline is not straight, the peak of largest absorption intensity is found by consideration of both the base and the peak height.

7. Remove the sample and sample holder and replace the 1 cm cuvet sample holder in the instrument, using the screw to secure it properly.
8. Be sure you have screenshots of the needed results, and the Excel spreadsheet generated at the end of the run. Exit the software and turn off the instrument.

Instructions for Data Analysis (Part I Absorption Spectra of Iodine)

Note

- Do not forget to make corrections to the wavelengths based on the results of the validation experiment.
- Be careful not to confuse peaks originating from $v'' = 0$ with those of "hot bands" originating from $v'' > 0$.
- You may consult your instructors and classmates during data analysis, however all work submitted for grading should be your own.

1. Given that the $v'' = 0$ to $v' = 25$ transition occurs at 545.5 nm, assign the peaks in the spectrum according to their v' values.
2. Choose 20 peaks:
   - Convert their wavelengths to wavenumbers. These are the values of G_v.
   - Calculate $\Delta G_{(v)}$ (see Equation 5.3.5)
3. Using MATLAB or another program, plot $\Delta G'_{(v)}$ (wavenumbers) vs $(v' + 1)$ (see Equation 5.3.5). Perform a linear least squares regression and overlay the fitted line on the plot of the data.
4. From the intercept calculate ω'_e using Equation 5.3.5.
5. From the slope calculate χ'_e using Equation 5.3.5.
6. From Equation 5.3.7 calculate D'_e.
7. Estimate your error in measuring the peak positions. Using the standard deviation of the slope and intercept, and Equation 5.3.5, calculate the uncertainties in ω'_e, χ'_e and D'_e.
8. Calculate the Morse parameter, a' from equation Equation 5.3.7.
9. Compare your results with literature values (Ref. 8, p. 540, and Ref. 4).

Discussion Questions

Note

For the following questions, you will need to have already done the data analysis for Part II.

Include responses to the following in your ELN.

1. Determine the value of ν_{00} (the energy of the transition from $v'' = 0$ to $v' = 0$ is notated by the symbol ν_{00}).
   - Use Equation 5.3.4, which is copied below for convenience, to find $G_{(v'=0)}$ and $G_{(v''=0)}$:
     $G_v = \omega_e \left(v + \frac{1}{2}\right) - \omega_e \chi_e \left(v + \frac{1}{2}\right)^2 + \ldots$ parameters.
   - Using Equation 5.3.8.: $\nu_{(v'',v')} = \nu_{el} + G_{(v')} - G_{(v'')}$.
2. Why do the vibrational spacings get narrower as V(R) increases?
3. Why is the Morse potential asymmetric?
4. Why are some of the transitions called "Hot Bands"?
5. How would you calculate χ''_e and D''_e using the hot bands?. (See reference 6 for help.)
6. What are the units of the Morse parameter, a, in Equation 5.3.7?

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6.5: Experimental Part II - Emission Spectrum of Iodine Vapor

In this part of the experiment you will use a HeNe laser at 543.5 nm to excite iodine to the B state, and a monochromator and photomultiplier to measure the spectrum of the emission back to the ground X state. It is worth noting that this technique of "laser-induced fluorescence" is an important spectroscopic tool, not only for physical chemists, but also for analytical chemists. The sensitivity is extremely high, and this has led to a wide variety of applications. These include the measurement of trace amounts of osmium and iridium in rock samples as part of an effort to test a theory for the sudden destruction of the dinosaurs by a catastrophic collision of the earth with an asteroid!

Laser Safety

Since the laser used in this experiment can be harmful, and the apparatus is relatively expensive, a number of safety precautions must be taken.

Safety and Other Precautions

1. **Don't look into the laser!** This is a class IIIa/3R laser. If the beam is directed into your eye it will damage your eye before you can blink. However you will still want to avoid looking directly into the beam, or having the beam be directed at you. Any glass that the laser hits will reflect about 5% of the beam intensity. This specular reflection may accidentally be directed toward your eyes. **Therefore, do not move items into or out of the laser path with the laser on. Wear laser goggles whenever the laser is on.**
2. Don't vent the cell. There is no danger to you if you vent it, but you won't be able to do the experiment until the cell is evacuated again.
3. Don't kill the PMT. The Photomultiplier Tube (PMT) is an extremely sensitive light detector. If you can see the light, that's enough light to overload the PMT if there is voltage on it. Read and understand the experimental procedure before applying any voltage to the PMT. Do not turn on the voltage to the PMT if it is exposed to significant amounts of light. Also, turn up the voltage slowly as you look for signal. As long as the observed signal stays below 0.2 V the PMT will not be damaged. Again, no physical damage to you will result from overloading the PMT, only financial.

Note

The Helium-Neon laser frequency of 543.5 nm corresponds to one of the larger absorption peaks from the absorption spectrum obtained in Part I of the experiment. Notice that absorptions close to 543 nm in the absorption spectrum (Part I) are among the most intense absorptions.

Preparation of Gas Sample Cell

- A cell containing solid iodine (I_2) will be put under high vacuum to vaporize the I_2 for spectroscopic analysis.

Vacuum-Line Start-Up

Some of the following may be completed by the TA before the lab period.

1. Check that all external valves on the working and main manifold are closed to the outside atmosphere.
2. Attach an empty N_2 trap to the main manifold. *Hold this trap in place until a vacuum has formed.*
3. Turn on the floor vacuum pump to start generating a vacuum.
4. Turn on all valves in the manifold that are connected to gages (marked with purple tape).

5. Turn on the diffusion pump.
    - Ensure that the floor pump is on BEFORE the diffusion pump. Otherwise, the diffusion pump will generate heat and the oil within the pump will oxidize, causing long-term damage to the diffusion pump.
6. Turn on Digivac electronic monitor. Use this to actively monitor the pressure at the end of the main manifold.
7. Check the analog pressure gauge on the diffusion pump to ensure the pressure is stable.
    - Throughout the experiment, the pressure should remain near 10 mtorr if the system is closed and stable.
8. Fill a 4L dewar with liquid N_2 from the shared Chemistry department supply.
9. Place a second dewar underneath the N_2 trap on the Main Manifold and fill with liquid N_2 such that the N_2 trap is submerged in liquid N_2.
10. Place the iodine trap on the main manifold and place a third (small) dewar under the trap such that the trap is submerged.
11. Check the level of N_2 as the experiment progresses. Refill if necessary to ensure the trap remains cold.
12. Check to ensure the pressure at the end of the main manifold is near 10 mtorr before proceeding.

1. Use the high vacuum line, with help from your TA, to evacuate the iodine vapor cell that will be used in the emission experiment.



Figure 6.5.1: A sample cell containing solid iodine is placed in a liquid nitrogen dewar and evacuated using the main manifold of a high vacuum line. (CC-BY-SA; Kathryn Haas, Duke Chem)

2. Once the cell is well evacuated, place it on the sample holder on the laser table. The cell should be in the path of the laser and there should be nothing obstructing the light path.

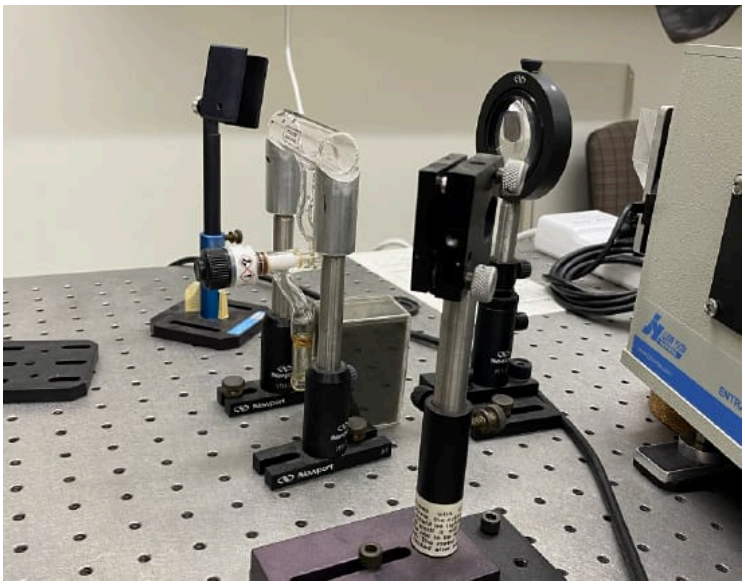


Figure 6.5.2: A sample cell is positioned on the sample cell holder in the path of the laser. The valve on the sample chamber is positioned toward the laser and away from the detector, as shown. (CC-BY-SA; Kathryn Haas, Duke Chem)

Vacuum Line Shutdown

1. Turn off the diffusion pump. Wait 5 mins for the pump to cool.
    - The pump should be cool before any oxygen is introduced to the system to prevent oil in the pump from oxidizing.
2. Close all valves with purple tape.
3. Turn off Digivac monitor.
4. Turn off the floor pump.
5. Pick an external valve and open it to release the vacuum and open both the working manifold and the main manifold to the air.
    - Do this quickly after step 4. The system should not be left under vacuum without an active vacuum pump.
6. Remove N_2 trap and transfer it to the fume hood to safely evaporate excess HCl/DCl gas.
    1. Do this quickly after step 5. Leaving the N_2 trap cold after the vacuum has been released may cause liquid O_2 to condense, which is highly volatile.

Instrument Configuration

The figure below shows a schematic diagram of the instrument set up.

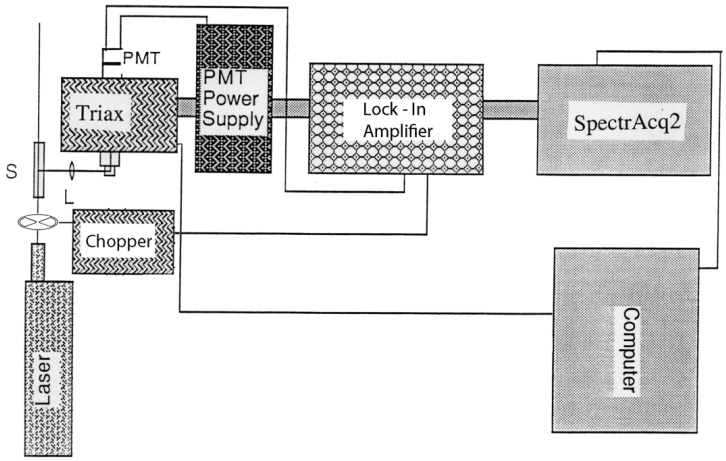


Figure 6.5.1: Instrumentation used for Laser Fluorescence Experiments. (CC-NC-BY-DUKE CHEM)

Laser: A Research Electro-Optics, Inc. HeNe laser (model 30968), which emits visible light (543.5 nm), is used to pump primarily transitions from $\upsilon'' = 0$.

Monochromator: A Triax 320 monochromator is used to disperse the emission signal from the sample. The entrance and exit slits of the monochromator control the signal intensity and resolution. It is best to use very narrow slits when looking for signal of unknown intensity so you don't overload the photomultiplier tube (PMT) detector with too much light. The PMT is mounted on the exit slit, which should be set to the same width as the entrance slit. There is a slide shutter on the exit port. The manual control unit (CD-2a) can be used for tuning the monochromator when you are setting up the experiment. The monochromator is computer controlled during data collection.

PMT Power Supply: The PMT power supply allows you to introduce a voltage to the PMT. Typically you will use a voltage off 1100 volts for this specific PMT. Depending on the available time, your TA may show you the effect of PMT voltage on the observed signal.

Lock-In Amplifier: In association with Stanford Research Systems (SRS) chopper an SRS510 Lock-in Amplifier is used to improve the signal to noise ratio of the emission spectrum. The interested student should read the Bentham Instruments introduction to the principles of a lock-in amplifier in the Course Documents section of your Sakai site, or at http://www.bentham.co.uk/pdf/F225.pdf.

Spectra Acq2: This is an analog to digital (A/D) converter which takes the analog signal (current from the PMT) and converts it to a digital signal that the SynerJY computer software can read and process.

Operating the Laser Spectrometer

1. Turn on the Chopper using the power switch on the back of the power supply. It should already be set to approximately 500 Hz. If necessary, adjust settings using the frequency adjust controls to bring it to approximately 500 Hz.

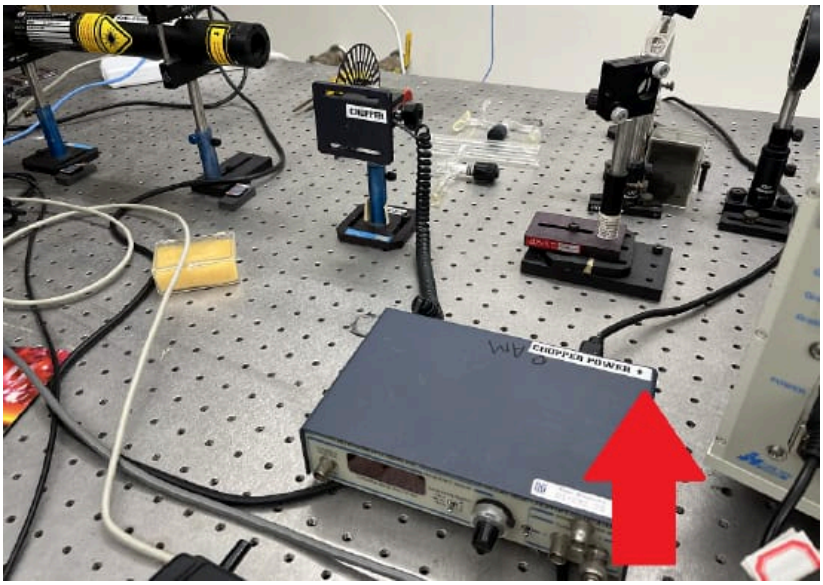


Figure 6.5.3: The chopper and its power supply are labeled. Turn on the chopper using the switch on the back side of the power supply. (CC-BY-SA; Kathryn Haas, Duke Chem)

2. Turn on the power for Amplifier and Photomultiplier Tube (PMT).
   a. Turn on the Pre-Amp power supply using the toggle switch on the box.
   b. Turn on the Lock-in Amplifier using the black switch on the front right of the box.
   c. Turn on the PMT Power Supply, but do NOT apply voltage yet.



Figure 6.5.4: **a) The Pre-Amp power supply** is the black box in the center of the picture; it is turned off using the silver toggle switch. **b) the Lock-in Amplifier** is the box on the left of the photo; it is powered on using the black toggle switch at the bottom right of the control panel. **c) The PMT power supply** is the box on the right; it is powered on using the press button at the bottom right. Do NOT touch the black switch to apply voltage to the PMT until the lights in the room are off. (CC-BY-SA; Kathryn Haas, Duke Chem)

3. Turn off the lights in the room.
4. With the lights off, turn on the laser (key on the laser power supply). Notice that while the laser beam itself is green (543.5 nm), the emitted light, seen as a beam along the length of the sample cell, is in the yellow orange, that is, at lower energy (higher wavelength) than the exiting laser. Of course what you see in the cell is the sum of all wavelengths of emitted light. To resolve that into a spectrum, you will send that light into the monochromator and scan an appropriate wavelength range.
5. Click the SynerJY icon (

) on the computer screen to load the SynerJY software.
6. From the **Collect** menu choose **Experiment Setup**.

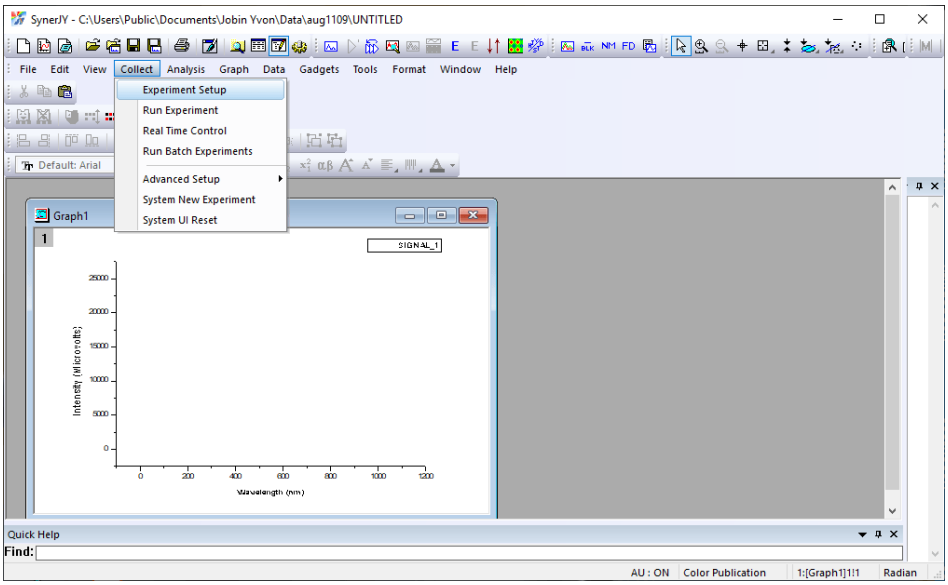


Figure 6.5.5: Choosing Experiment Setup from the Main SynerJY Window. (CC-NC-BY-DUKE CHEM)

- Now, just wait until the system initializes. You will briefly see two windows come and go as the software connects with the monochromator. The first to appear is a **Hardware Configuration** window, and **Triax320PMT** should be highlighted in it.

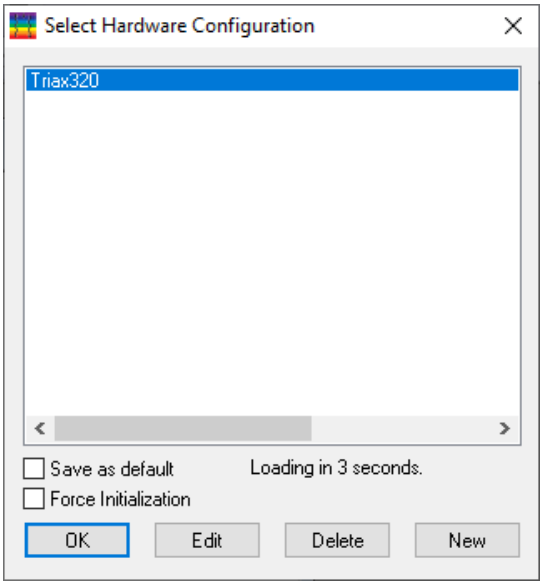


Figure 6.5.6: Hardware Configuration. (CC-NC-BY-DUKE CHEM)

- This window will disappear and be replaced by an **Initialization** Window. The software will initialize the monochromator and PMT and then that window will also disappear.

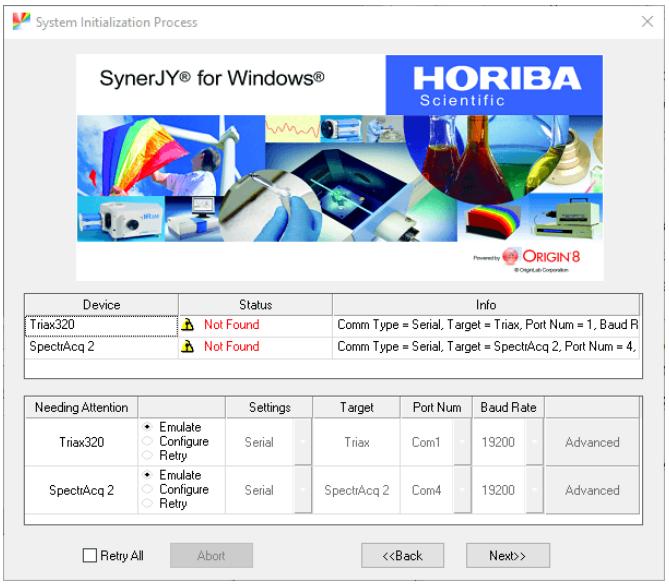


Figure 6.5.7: The Initialization Window. (CC-NC-BY-DUKE CHEM)

- The software will then load the Experiment Setup screen.

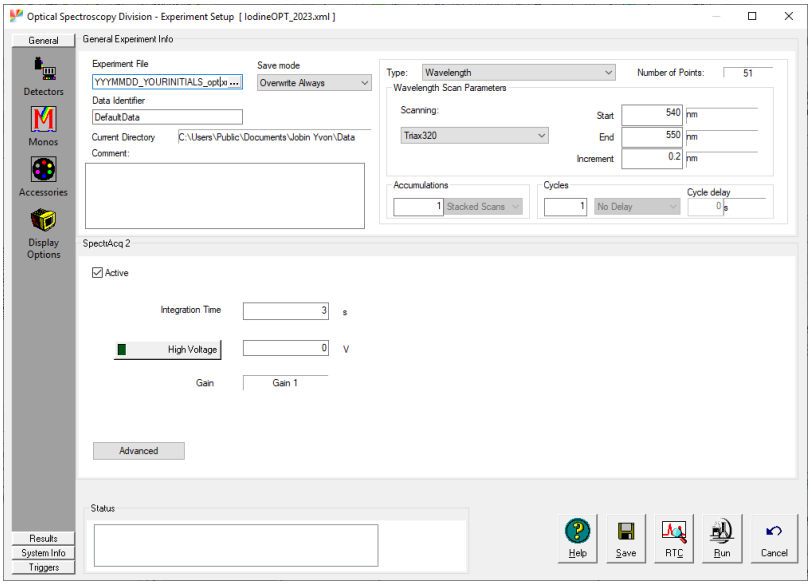
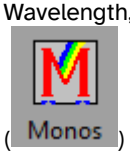
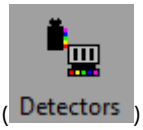


Figure 6.5.8: The Setup Screen. (CC-NC-BY-DUKE CHEM)

7. **Set up the optimization experiment:**
   a. Type a name for your **Experiment File** (use YYYYMMDD_YourInitials_opt).
   b. Press **SAVE**.
   c. Choose a **Start Wavelength of 540 nm** and an **End Wavelength of 550 nm**.
   d. Set the **Increment** to **0.2 nm**.
   e. Make sure **Type** is set to Wavelength, and **Triax320** is selected under **Scanning**.
   f. Click the "Monos" button (

) at the left of the screen and set the **Front_Entrance** and **Front_Exit** Slits each to **0.026 mm**.
   g. Click on the Detectors button (

) button at the left of the window and make sure there is a check in the PMT **Active** box and set the **Integration Time** to 3000 ms (i.e. 3 seconds). Leave the **Gain** at x1.

8. **Turn on the PMT**
   a. Using the buttons on the PMT power supply, apply 900 volts to the PMT. Do this by typing "900" and then pressing the "Enter" button. Then switch the power to "on".
   b. On the software, click on the Real Time Control button (RTC, 

).



Figure 6.5.9: Real time controller. (CC-NC-BY-DUKE CHEM)

   c. Make sure the Slits and Integration Time are set properly.
   d. Change the value in the **Position** box to 543.5 nm.
   e. Click on the "Run" button (

).
   f. Wait a few seconds, then look at the digital readout on the lock-in. You should see less than a tenth of a millivolt signal at this point.
   g. Repeat the steps above to change the PMT voltage to 1000 V and watch the signal at the lock-in. Make sure it does not go off scale; decrease the sensitivity if needed.
   h. Bring the PMT voltage up to 1100 V, adjusting the lock-in sensitivity to obtain a good signal (several tenths of a mV) without going off scale.
   i. Click the "Cancel" button (

) to return to the main Experiment screen.

9. **Run the optimization Experiment:** Click on the "Run" button (

) to start the short optimization experiment. You will see the spectrum appear in the Display window as the scan progresses. You should see a peak at the pump wavelength. When the scan is complete you may be asked about saving files. To be safe, save all files when asked. Your scan will then appear in the main window of the SynerJY software (Figure 6.5.10).
10. Double Click on the spectrum so that you can edit it. Then select **Pick Peaks** from the **Analysis** menu.

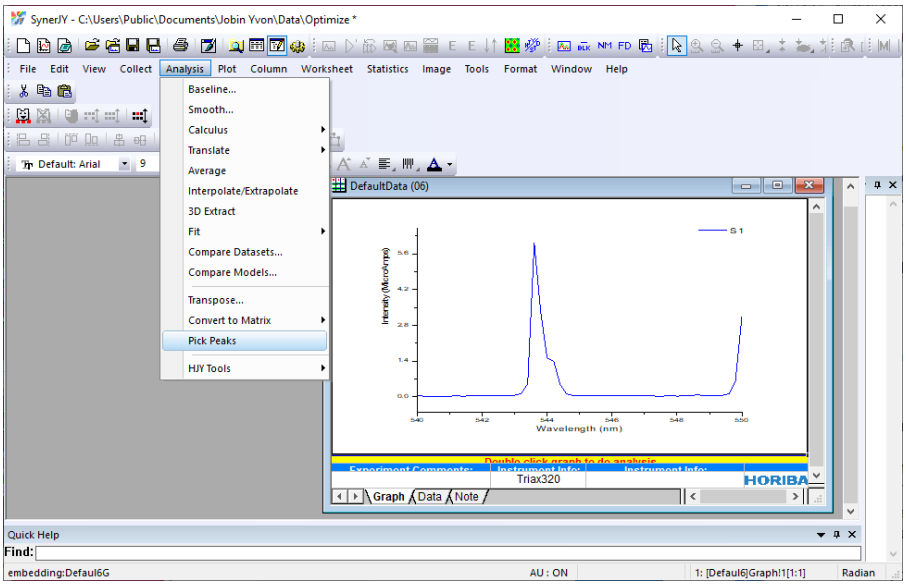


Figure 6.5.10: The Results of the Test Scan. (CC-NC-BY-DUKE CHEM)

a. To begin the peak analysis leave the default settings in the boxes and select **Find Peaks** at the bottom of the **Peak Analyzer** window. Then press **Finish**.

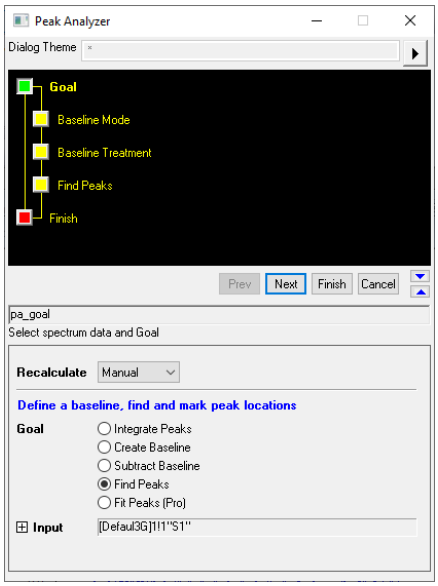


Figure 6.5.11: Copy and Paste Caption here. (Copyright; author via source)

b. If you do not like the results, alter the Height and Width values until you get a good result. In the example shown in Figure 6.5.10 the major peak is found at approx. 543.5 nm, demonstrating that our system is working properly.

11. Do any final optimizing of the signal (check with your TA) and start the run.
12. **Create the Iodine Emission Experiment:**
    a. Make sure the **Increment** is set to 0.2 nm.
    b. Make sure the **Integration Time** is still set at 3000 ms.
    c. Change the **Start** wavelength to 510 nm and **End** wavelength to 800 nm.

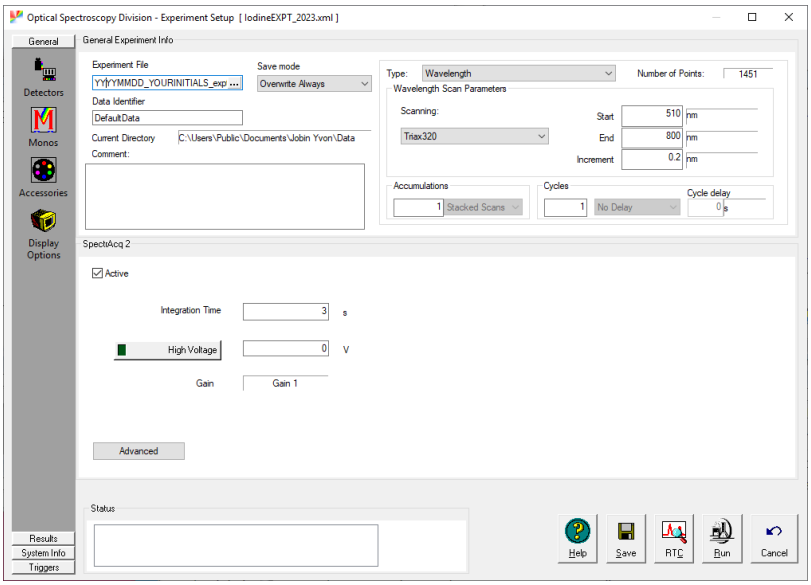
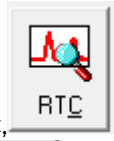
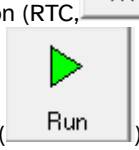


Figure 6.5.12: Setting Up The Sample Run. (CC-NC-BY-DUKE CHEM)

d. Click the Real Time Control button (RTC, 

) to set the monochromator to the start wavelength.

e. Click the **Run** button ONCE only (

) and wait a few seconds (this is equivalent to setting the monochromator to the start wavelength and allowing the detector signal to relax).

f. Then click the **Cancel** Button ONCE only (

) to return to Setup screen.

g. Click the "Run" button (

) from the setup screen to start the full scan.

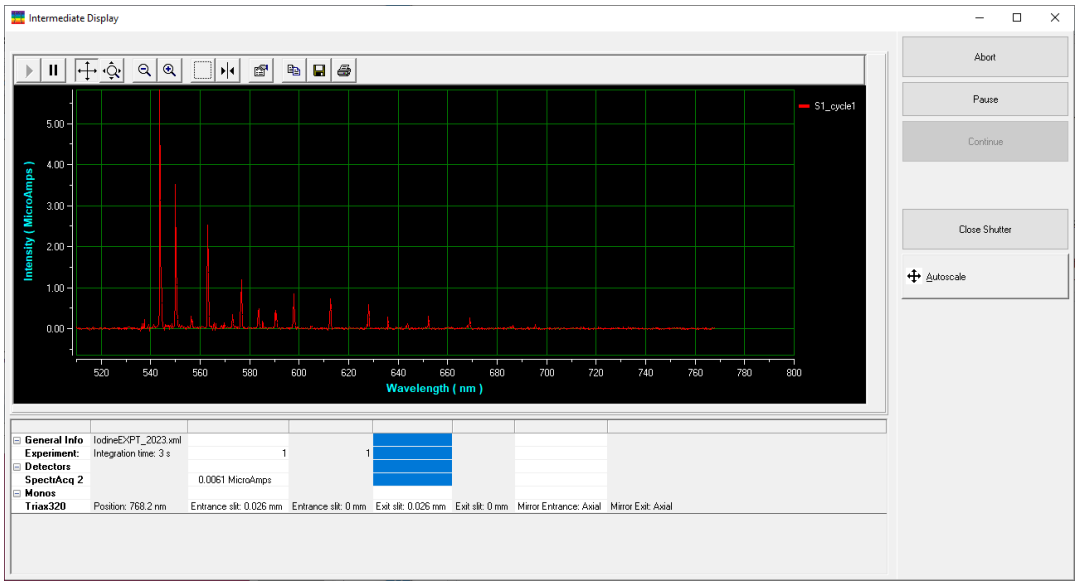


Figure 6.5.13: Data collection. (CC-NC-BY-DUKE CHEM)

h. Watch the data collection for the first 5-10 minutes to be sure everything is running correctly. The total scan will take a at least 1.5 hours. If you leave the room, close the door behind you to be sure that stray light does not get into the experiment.

13. At the end of the scan you may want to rescale the horizontal axis to see the spectrum more clearly.

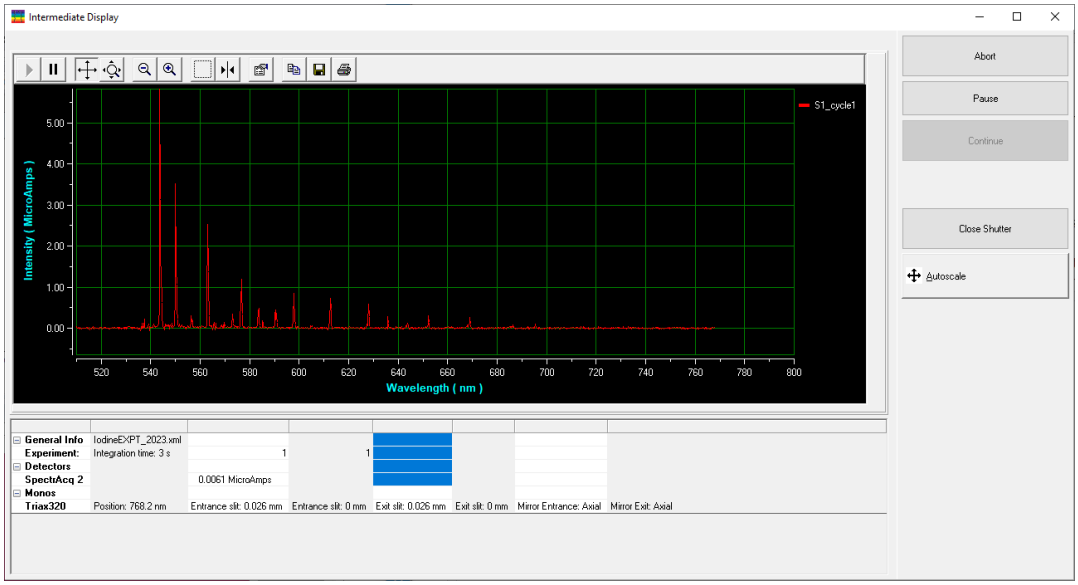


Figure 6.5.14: The FInal Spectrum. (CC-NC-BY-DUKE CHEM)

14. Repeat the Pick Peaks procedure you did earlier on the short scan. Likely you will need to adjust the parameters in the Pick Peaks dialog box to get most or all of the peaks. Below is a suggested set of options:
    a. Goal: **Find Peaks**
    b. Baseline Mode: **Constant, Median**
    c. Baseline Treatment: **Auto subtract baseline**
    d. Find Peaks: **Enable Auto Find, Peak Filtering By Height, Threshhold at ~ 1-2%**
15. When you get a good listing of the peaks look at the bottom of the data window where you will see a list of the files associated with these data (Figure 6.5.15). Click on the Peak_Centers1 worksheet and you will get a table of the peaks found in the spectrum.

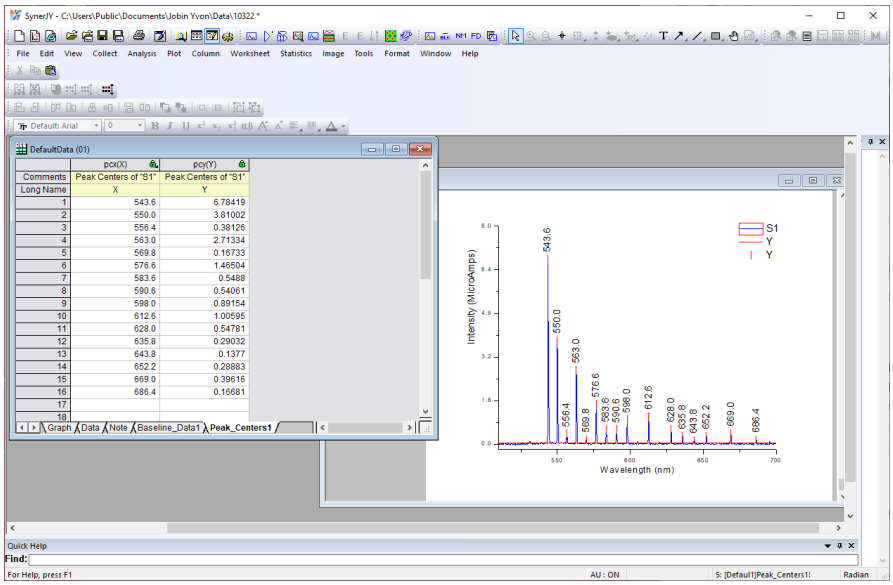


Figure 6.5.15: The Peaks Table. (CC-NC-BY-DUKE CHEM)

You can copy the appropriate data from there to an Excel spreedsheet. You should the save the spreadsheet and any screenshots that you need.

16. **Shutdown:**
    Before you shut down, be sure you have collected all necessary data in your ELN and in excel. Then Send a copy of the ELN to you and your partners.
    a. Turn off the laser using the key.
    b. Turn off the power to the PMT and power off the power supply.
    c. Turn off the power to the Pre-amp Power Supply
    d. Turn off the power to the Lock-in Amplifier.
    e. Turn off the Chopper.
    f. Close the SynerJY software.

Instructions for Data Analysis

You may consult your instructors and classmates during data analysis, however all work should be your own.

1. Assign at least 19 peaks in the emission spectrum based on the known pump transition. Remember, this is an emission spectrum. Longer wavelengths (lower energy) correspond to transitions from higher ground state vibrations.
    a. Convert the wavelengths of these peaks from nm to wavenumbers.
    b. Create a Birge-Sponer plot (see Equation 5.3.5) by plotting $\Delta G''_{\upsilon}$ vs $(\upsilon'' + 1)$.
2. From the intercept of the Birge-Sponer plot, calculate ω''_e (using Equation 5.3.5).
3. From the slope of the Birge-Sponer plot, calculate χ''_e (using Equation 5.3.5).
4. From the Morse Potential (using Equation 5.3.7), calculate D''_e.
5. Estimate the uncertainty in the peak positions using the standard deviations from the least squares analysis and calculate the uncertainties in ω''_e, χ''_e and D''_e.
6. For comparison, calculate the value of D''_e using Equation 5.3.9 as follows: From the wavelengths of at least three absorption lines, calculate the corresponding transition energies $\nu_{(\upsilon'',\upsilon')}$ (where $\upsilon'' = 0$) in units of cm^{-1}. For these same transitions, calculate $(G_{(\upsilon')} - G_{(0'')})$ using Equation 5.3.4 and your values of ω''_e, ω'_e, χ''_e and χ'_e. Now use Equation 5.3.8 to calculate the average value of ν_{el} for the three transitions. Finally, use Equation 5.3.9 and your value of D'_e from Part I to calculate D''_e. The value of E(I*) is known to be 76003 cm^{-1} from atomic spectroscopy.[1] Which value of D''_e has the least uncertainty (neglect the error in E(I*))?
7. Calculate the Morse parameter (a") from Equation 5.3.7.
8. To plot the Morse potential wells, you will use the Matlab routine ***morse***. Simply type ***morse*** and follow the screen prompts. Separate ground and excited state Morse potential curves will be plotted using your experimental data, and sent to the printer. For now, both R''_e and R'_e are set at zero. Vibrational quantum levels will be shown for both ground and excited states.
9. The maximum intensity in the absorption spectrum occurs as the excited state vibrational wave functions overlap vertically with the ground state wave functions. A Matlab script, ***overlap***, is used to overlay the two plots and shift the ground and

excited state potential wells such that the center of $v'' = 0$ overlaps with the left edge of the $v' = 25$. At the Matlab prompt type ***overlap*** . The script will animate the overlap of the ground and excited states and the vertical transition. It will also estimate the displacement ($R'_e - R''_e$) (Ångstroms) between the minima of these two potential wells along the R-axis. Save a copy of this graph (or take a screenshot) for your ELN, and record the displacement.

> **Note**
>
> The ground and excited state potential wells are overlaid so that the displacement $R'_e - R''_e$ may be measured. However, this gives a misleading impression of the relative positions (energies) of the two potential wells. Clearly the excited state potential well is at much higher energy than the ground state potential well (see Figure 5.3.3 and note the discontinuity in the V(R) axis). A realistic picture is shown in reference [10]. In the Introduction to Matlab Excercises, you plotted the ground and excited state potential wells for iodine using literature values for D_e, a, and R_e. You will now repeat this assignment using your results.

10. The functional form of the Morse potential may be represented by the equation

$$V(R) = T_e + D_e \left[1 - e^{-a(R-R_e)}\right]^2 \tag{6.5.1}$$

where T_e is the electronic term energy (the energy at the bottom of the potential well). T''_e and T'_e represent the electronic term energies of the ground and excited states respectively. If we set $T''_e = 0$, then $T'_e = \nu_{el}$. Given that $R''_e = 2.66$ Å (obtained from IR spectroscopy), calculate R'_e using your value of $R'_e - R''_e$.

11. You will now use your values of T''_e (zero), T'_e ($= \nu_{el}$), D''_e, D'_e, a", a', R''_e and R'_e to replot the Morse potential wells for the ground and excited states of iodine on the same graph. Return to your Matlab command window, and as instructed, press any key to continue. Enter your calculated T'_e. The two Morse potentials will be plotted on one graph and the vibrational quantum levels will be shown for both ground and excited states. Save a copy of this graph (or take a screenshot) for your ELN.
12. Compare all of your results with literature values (See, for example, reference. 1, p. 430-432).

Discussion Questions

Include discussion of the following in your ELN.

1. Why are the vibrational spacings different in the ground and excited states?
2. Why is the shape of the Morse potential different in the ground and excited states?
3. How is it possible to observe emission peaks at higher energies than the pump energy?

This page titled 6.5: Experimental Part II - Emission Spectrum of Iodine Vapor is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

6.6: References and Additional Reading

Duke students can find additional reading materials at the link below, many of which are listed in the references below.

Duke students, click here for additional readings, or find the resources below in the Library (yes, the physical library!)

References

1. Shoemaker, D.P., Garland, C.W., Nibler, J.W., Experiments in Physical Chemistry, 6th ed., McGraw-Hill, NY, 1996, Chapter XIV, Experiment 40.

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10. Lievin, J., *J. Chem. Ed.*, **1982**, 59(9), 777.

11. Baxter, G.P. and Grose, M.R., *J. Amer. Chem. Soc.*, **1915**, 37, 1061.

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7: MOLECULAR ELECTRONIC STRUCTURE CALCULATIONS

7.1: Pre-Lab Assignment

7.2: Introduction to Electronic Structure Calculations

7.3: Accessing Spartan

7.4: Exercise 1 - Estimation of the IR Spectrum of HCl, and Comparison of Basis Sets

7.5: Exercise 2 - Molecular Orbitals of Formaldehyde

7.6: Exercise 3 - Modeling Sulfur Dioxide - Comparing the Results of Different Basis Sets and Calculation Models

7.7: Exercise 4 - Modeling the Absorption Spectrum of Cyanine Dyes

7.8: Exercise 5 - Modeling an Intramolecular Rearrangement

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7.1: Pre-Lab Assignment

Pre-Lab Assignment

Complete the general pre-lab assignment for this module. This module is an introduction to computational chemistry and molecular electronic structure calculations using Spartan software. These computational exercises circle back around to some of the "wet lab" modules you completed earlier in the semester.

To help you prepare for this modulewe ask that you do the following:

1. Read the introduction to the lab, and the chapters in your textbook on quantum mechanics and electronic structure theory for molecules.
2. Briefly read the Guidelines for Using Spartan® Software and look over some of the supplemental reading materials provided.

Planning ahead for your Independent Project

The Spartan exercises will be followed by an independent project in which you can choose to do a computational study.

We ask that you begin to think about your independent project, and we want you to do something you are really interested in! In 310L, you can choose a topic for your independent project, and choose whether you would like to dive into more computational work, or explore other applications of physical chemistry in the peer-reviewed literature. You should begin searching the literature (eg using Web of Science or looking at the Table of Contents for leading Physical Chemistry journals) for physical chemistry topics that interest you. Alternatively, you can think about simple chemical phenomena or reactions that you are interested in and that you can model using Spartan. Come to the laboratory session prepared with a brief written proposal (1 paragraph) on at least two ideas for what you might do for your independent project and be prepared to discuss it with your instructors.

Introduction

Computers and computational methods have become major tools of chemical research. This comes from the availability of powerful workstations and software packages at affordable prices, the development and implementation of accurate and efficient computational theory, and the insight and user-friendly interface provided by scientific visualization.

In this laboratory exercise, you will use the Spartan® software to explore the calculations of properties of isolated molecules based on a whole range of modeling methods, from empirical molecular mechanics to accurate *ab initio* quantum mechanical methods. You will carefully study the accuracy of each method by comparison with experimental results and with other computational methods. Understanding the limitations of modeling methods is as important as knowing their availability and accuracy. We will learn how such techniques can be used to help solve chemical problems.

There are two parts to the Spartan Exercise:

1. The first part of the exercise is designed to relate to the previous "wet lab" modules of this course.
2. The second part focuses on using computational methods to gain knowledge that is difficult to get from experimental methods; that is to study frontier molecular orbitals and transition state structure in chemical reactions.

> **Note**
>
> This lab is split into 5 separate exercises designed to illustrate the various capabilities of Spartan. The requirements for your lab notebook are stated within each exercise instead of at the end of the chapter. It is recommended that you follow along with the ELN template while completing this lab to ensure that all data is properly recorded.

Independent Project

This is for *Chemistry 310L students only (301L students don't need to do this)*. After completing the Spartan excecises, you will porpose and complete an independent project - for this project, you are welcome to model your own favorite molecules or reactions. You will need to design this part of the project before you come to the laboratory and learn to ask the right questions with the proper tools. This is an opportunity to explore something that is interesting to you.

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7.2: Introduction to Electronic Structure Calculations

Calculation of the electronic structure of a molecule (i.e. the molecular orbitals) can be accomplished by the following steps:

1. **Preparation of the input data**: Within the Born-Oppenheimer approximation, nuclei are held fixed while solving for the *electronic* motion. Before you begin your calculations, you must first define the fixed nuclear positions at which the electronic structure calculation will be performed -- i.e. you must define a molecular geometry. In Spartan®, this is done graphically in much the same way in which you built molecules when you took organic chemistry courses.

   Many of the calculations you undertake here will use a variational approach in which the molecular wavefunction is written as a single Slater determinant of molecular orbitals (MO), where each MO, in turn, is written as a Linear Combination of Atomic Orbitals (LCAOMO). To begin this variational approach, you must obtain a starting "trial wavefunction." In the LCAOMO method, this requires definition of the atomic functions that will be used to construct the MO's. Recall the variational approach to the electronic structure of H_2 -- to begin we used a trial LCAOMO wavefunction Ψ written as a linear combination of a 1s atomic orbital on HA (Φ1sA) and a 1s atomic orbital on HB ((Φ1sB); i.e., we defined the atomic functions that were used to construct the MO's. In Spartan® you will find a reasonable collection of such sets of atomic functions built into the software, and consequently, selection of an appropriate set of atomic functions is usually achieved by simply choosing from a selection of available methods and basis sets.
2. **Running the calculation:** After building the molecule of interest and selecting the type of calculation to be run, and other relevant parameters, one submits this job for calculation.
3. **Analysis of the results**: This may involve such tasks as viewing electron densities, exploring the bonding or antibonding character of molecular orbitals, animating vibrational modes associated with nuclear motion, viewing energy-minimized structures and determining bond lengths and bond angles, or calculating molecular properties. Most of this analysis is done using the graphical interface available in Spartan® thereby minimizing the need to examine multiple pages of numerical data! Again, Spartan® simplifies the analysis by providing numerous visualizations and menu-driven data displays.

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7.3: Accessing Spartan

A network version of Spartan 20 is available from the chemistry server, bohr. Access to Spartan through FastX is the same as access to Matlab, except that you will want to type...

```
spartan
```

at the prompt after logging in. Every computer in the physical chemistry lab is already set up with FastX. In addition, you will likely want to have access from your own laptop. Complete instructions for obtaining and configuring FastX, and the Duke VPN (if needed) can be found here.

1. Loading – Spartan® 20



1.1. Click the FastX shortcut icon, on the main screen of any computer in the Advanced Labs. Click on the bohr.chem.duke.edu session. Enter your NetID and password and click Continue. Click on the + at the upper right of the new screen that appears, and click on Xterm. An xterm window should appear. Find your TA or your Instructor if there are problems connecting; it happens sometimes.

2. Type

```
spartan
```

This will start the Spartan program and the main screen will appear.

Notice the menus and buttons at the top of the screen.

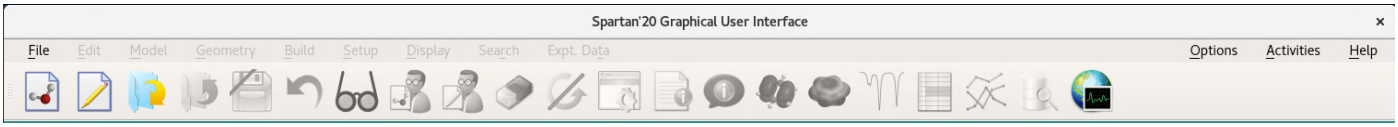


Figure 7.3.1: The Spartan Menu and Button Bar. (CC-NC-BY-DUKE CHEM)

You will use these menus and button to operate Spartan®. Note also the **Help** menu to the right of the menu bar. Among the many useful things included in the Help menu is a summary of mouse commands (within General Operating Features). You will use this summary frequently as you do your work.

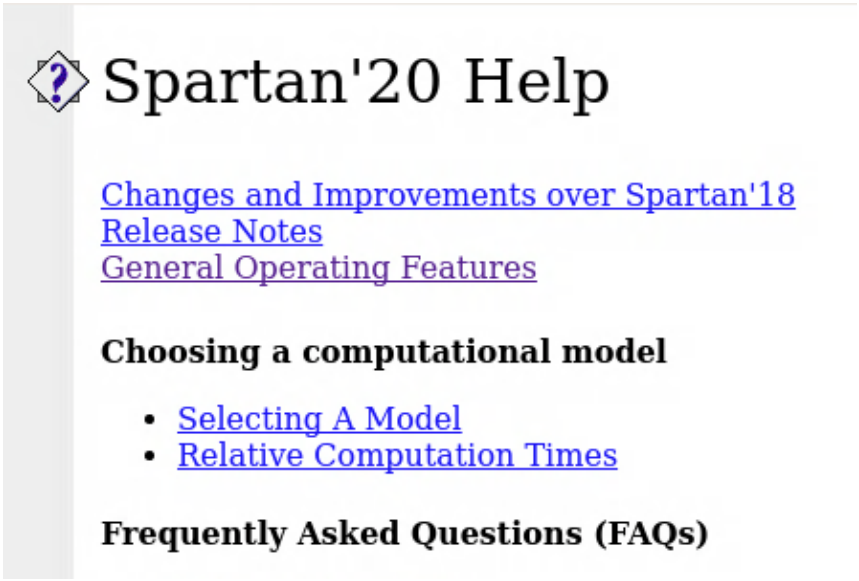


Figure 7.3.2: Spartan Help. (CC-NC-BY-DUKE CHEM)

Once in General Operating Features, scroll down to find the table of mouse functions.

Using the Mouse
The following functions are associated with the two-button mouse.

keyboard	left button[a]	right button[a]
-	picking, X/Y rotate	X/Y translate
Shift	range picking, Z rotate	scaling[b]
Control	multiple picking, global X/Y rotate[b]	global X/Y translate
Control + Shift	global Z rotate[c]	scaling[b]
Alt	group picking, bond rotation	bond stretching
Control ("Build" mode)	fragment X/Y rotate	fragment X/Y translate
Control + Shift ("Build" mode)	fragment Z rotate	scaling[b]

a) Left and right buttons together with no modifier keys are used for defining a section box.
b) Scaling is always applied to all open molecules and fragments. The **scroll-wheel** found can also be used for scaling.
c) Global rotations can be either molecule or screen centered. This is controlled by **Global Rotate** in the **Preferences** dialog (**Options** menu).

Mouse/keyboard operations may be broadly separated into two categories: selection (picking) and manipulation (translation/rotation).

Selection

Figure 7.3.3: Using the Mouse. (CC-NC-BY-DUKE CHEM)

Note

Spartan works best with a 3-button mouse. However it is easy enough to translate the mouse instructions to work equally well with a trackpad.

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7.4: Exercise 1 - Estimation of the IR Spectrum of HCl, and Comparison of Basis Sets

Note

These Exercises should be completed **individually**. As always, you may work alongside of other students and discuss your results, however each student should open the software on a computer, complete the tasks, and complete the ELN individually. Submit your individual copy of the ELN at the end of this session.

The ELN template is available here (click).

The goal of this first exercise is to compare your experimental FTIR data from the HCl diatomic molecule with computational predictions, and to compare different basis sets.

Estimation of the IR Spectrum of $H^{35}Cl$ and $H^{37}Cl$

Select New Build from the File from the menu, or click the  button.

1. The right side of the screen is the *model kit*.

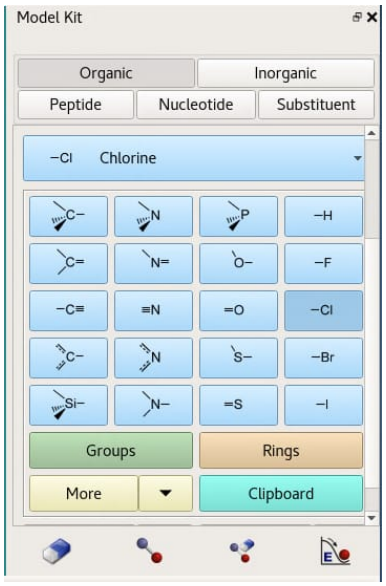


Figure 7.4.1: The Model Kit. (CC-NC-BY-DUKE CHEM)

Notice that you are in the **Organic** area of the model kit. Here you will see several common atom types and their hybridization. You might take a moment now to familiarize yourself with the other screens of the model kit, Inorganic, Substituent, Peptide and Nucleotide.

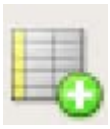
3. From within the Organic area of the model kit, click on the –Cl atom and then double-click somewhere in the working area of the main Spartan screen. You will see a colored line, with the Cl atom at the end. Select Save as from the File menu, or click

the  button. Keep the suggested filename, or give the file a name of your choice. A hydrogen atom is automatically added to your molecule. To see the hydrogen, click the  button to leave the Build Mode and enter the View Mode.

Note

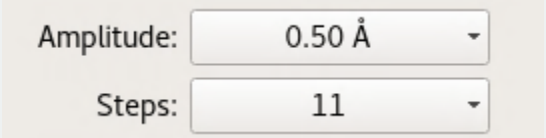
Clicking the  button returns you to the Edit Build Mode.

The exact view of the molecule will depend upon what "model" system you have selected. Use the **Model** menu to change how the molecule looks.

4. Select **Calculations** from the **Setup** menu. Choose **Equilibrium Geometry** at **Ground State** in **Gas,** *with* **Hartree-Fock, 3-21G**. *Total charge* should be **Neutral**, and *Unpaired Electrons* should be **0**. Select *compute*: **IR** (with Current Model). Click on **Submit**. If prompted, save the file (use the same file name). If everything is correct, you will see the "Job "*filename*" has been submitted" box. Click **OK**.
5. After a moment a "Job "filename" completed" box appears on the screen. Click **OK**. Inspect the output of this job using **Display**, **Output**. The **Summary** tab will give you the major results of the calculation. If you expand the **IR** section of the **Summary** you will see the calculated estimate of the frequency of vibration. Record this value in your lab notebook. In the **Output** tab, you will see information about the chosen basis set, the number of steps for geometry optimization, and other information related to the calculation. Close the **Output** dialog box. Then select **Spectra** under the **Display** menu and click on the , and select **IR Calculated**. The calculated spectrum appears on the screen. Click on the  and you will again see the harmonic oscillator frequency of HCl molecule.
6. To animate the vibrational motion, put a check in the box next to the frequency (or click on the peak in the spectrum). If you like, click on the  again and add the Experimental spectrum to the window. How well does the Hartree-Fock calculation reproduce the experimental IR spectrum? To stop the animation, click again on its frequency, or remove the check from the checkbox next to the vibration. Close the spectrum window.

Note

If the animated vibration is going too fast, the speed of the animation can be changed in the following way. Click on the  icon at the left of the spectrum display window. You will two editable buttons appear.



To slow down the animation, change the number of steps to a larger value (for example, 30).

Changing the Amplitude will alter the degree of displacement of the nuclei through the course of the vibration.

7. Back in the main window, under the **Geometry** menu choose **Measure Distance**, and find the H-Cl bond length by clicking on the two atoms (or by clicking on the bond between the two atoms). Look to the lower right corner of the screen to see the bond distance. Record the bond length in your lab manual and compare the result with your experimental and literature data.
   Click the  button to close your HCl file.
8. Make a new HCl molecule. Click the  to enter the View Mode. Click once on the chlorine atom to select it. Select **Properties** from the **Display** menu. An Atom Properties Box appears. Change the *Mass Number* from 35 to **37 (for ^{37}Cl)**. Close the Atom Properties box. Return to the Setup Calculations box and make configure the calculation to be the same HF calculation you did on HCl (do not forget to check the IR option). Click on **Submit**. Save the file under a new name and let the calculation run.
9. Find the harmonic oscillator frequency and the bond length for $H^{37}Cl$. Select **File**, **Close** to close your molecule when you are done.

Data for HCl	Calc. ν (cm^{-1})	Exp. ν (cm^{-1}) (FTIR)	Cal. Bond Length (Å)	Exp. Bond Length (Å) (FTIR)
$H^{35}Cl$				
$H^{37}Cl$				

10. Compare your results to those you obtained from the FTIR experiment done earlier in this course (specifically, for $H^{35}Cl$).
11. **Discussion Prompts:**
    What can you conclude about the accuracy of computing bond lengths and vibrational frequencies using this Hartree-Fock calculation?
    Why is the bond length identical for both $H^{35}Cl$ and $H^{37}Cl$?

Comparison of Basis Sets

Try the same calculation with a different basis set (6.31-G* for example), and/or a completely different model (semi-empirical or density functional). Does the accuracy of the results change?

Note

This section of your lab notebook should include:

- A table summarizing the results of the $H^{35}Cl/H^{37}Cl$ calculations
- Comparison of computational results to your experimental FTIR data and literature data
- What can you conclude about the accuracy of computing bond lengths and vibrational frequencies using this Hartree-Fock calculation?
- Why is the bond length identical for both HCl and DCl?

(See your ELN template for details)

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7.5: Exercise 2 - Molecular Orbitals of Formaldehyde

Exercise 2 - Molecular Orbitals of Formaldehyde

This experiment explores the capability of Spartan® to calculate Molecular Orbitals and construct corresponding surfaces. The formaldehyde molecule is used as a model.

1. Click  to start a new file.
2. Build H_2CO. Select **Carbonyl** from the **Groups** menu and double-click in the working area. You may want to rotate the molecule on the screen for a better view.

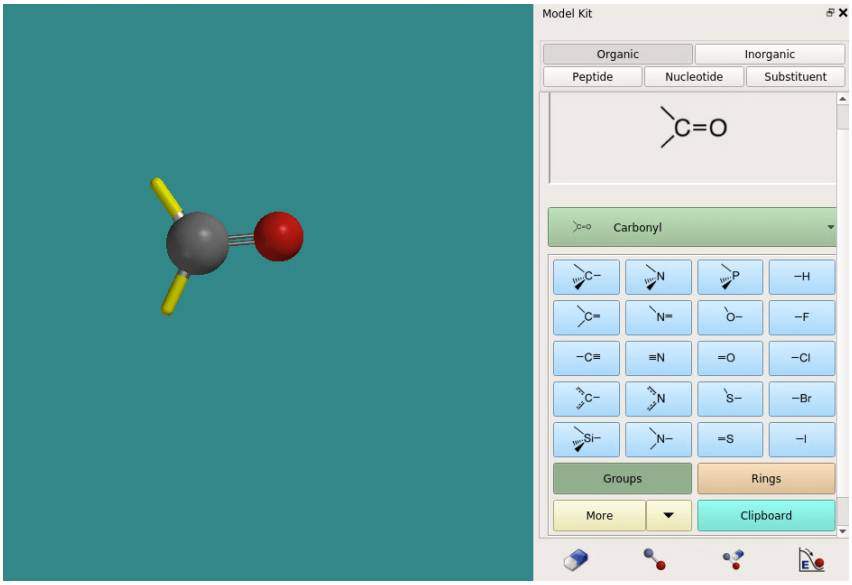
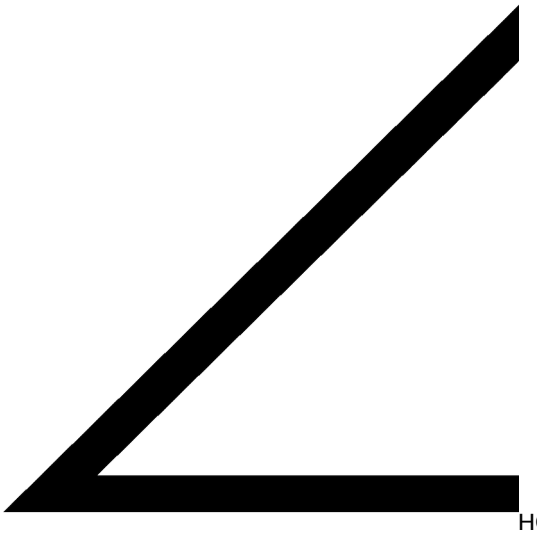
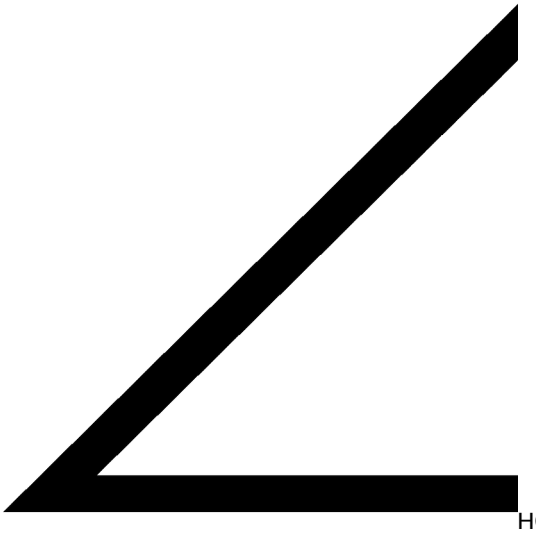


Figure 7.5.1: Building Formaldehyde. (CC-NC-BY-DUKE CHEM)

3. Click the  minimize button (lower right, below Clipboard).
4. Select **Setup, Calculations** from the menu. Choose **Equilibrium Geometry** at **Ground State** in **Gas,** *with* **Hartree-Fock, 6-31G***. *Total charge* should be **Neutral**, and *Unpaired Electrons* should be **0**. Click **OK**.
5. Choose **Submit** from the **Setup** menu. Click on the **OK** button. **Save** the file with the suggested filename, or choose one of your own.
6. Once the calculations have completed, determine the calculated equilibrium values for the C–O and C–H bond lengths,

and for the  HCH and  HCO bond angles, by using **Geometry, Measure Distance/Measure Angle**. Record these values in your lab notebook. Compare your calculated values with literature values.

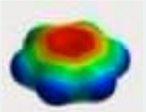
Note

The Computational Chemistry Comparison and Benchmark Database (CCCBDB) at NIST is one suggested place to look for this type of information. Choose an appropriate search string in your favorite web browser. For example: formaldehyde bond lengths and angles NIST. Look for the hit directing you to the CCCBDB site.

H_2CO	C=O length		HCO angle		HCH angle	
	Calc	Lit	Calc	Lit	Calc	Lit
Reference						

7. Inspect the Output of this job using the  button. Find the **Molecular Orbital Energies** section under the **Summary** tab. Calculate the energy difference between the HOMO and LUMO and record this in your lab notebook.
8. Click the  button to see an abbreviated MO diagram on the left side of the screen. From here you can click on an orbital to view it on the molecule. In this way find and visualize the π-bonding MO in H_2CO. You can change the appearance of the orbital display by changing the **Style** from Solid to Mesh to Transparent, etc. (at the lower right corner of the screen).
9. In the same way, visualize the LUMO surface. How might you describe this molecular orbital?
10. Now visualize the HOMO. How might you describe this one? Take a look at some of the other orbitals and record any other interesting observations (with images) in your lab notebook.

Note

Not every MO is shown in the diagram generated by clicking the  button. You can calculate the surface for any desired MO by clicking the  button, and *More Surfaces*. Then, from the *Surface* dropdown menu select **HOMO{-},N** or **LUMO{+},N**, where *N* is how many orbitals above the LUMO or below the HOMO needed to get to the orbital you wish to see. Click on **Apply**, and then **OK**. Put a check mark in the box next to the selected orbital and then return to the Spartan window to see the result.

Note

This section of your lab notebook should include:

- A table recording your calculated bond lengths and angles for formaldehyde and a comparison to literature values
- Calculation of the energy difference between the HOMO and the LUMO
- Images and descriptions of the HOMO, LUMO, and any other interesting orbitals of your choice.

(See your ELN template for details)

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7.6: Exercise 3 - Modeling Sulfur Dioxide - Comparing the Results of Different Basis Sets and Calculation Models

Exercise 3 - Modeling Sulfur Dioxide: Comparing the Results of Different Basis Sets and Calculation Models

This experiment is designed to explore the performance of various basis sets, models of *Ab initio* calculations and *Semi Empirical* calculations, and *Density Functional* calculations. The SO_2 molecule is used as a model.

1. Start a New Build.
2. To introduce you to another approach to building a molecule, select the **Inorganic** tab of the builder.
3. Build SO_2 as follows: Change the element to sulfur.

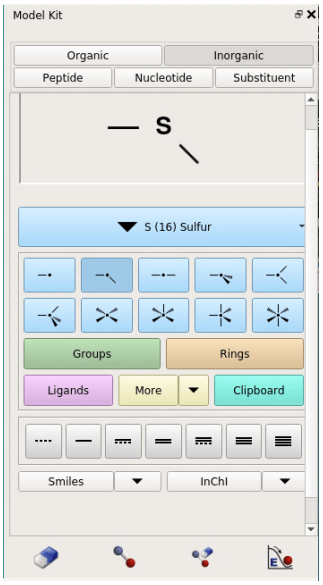
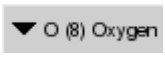
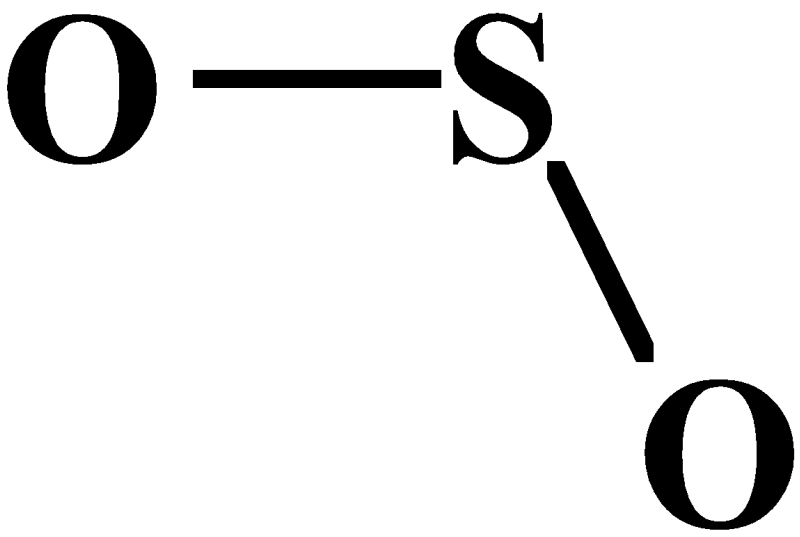


Figure 7.6.1: Selecting the Element Sulfur From the Inorganic Area of the Builder. (CC-NC-BY-DUKE CHEM)

Select  atom hybridization. Double-click in the working area. Rotate the molecule to make all the bonds visible. Select **O** from the periodic table 

and Select atom hybridization. Click at the ends of the bonds to **S** to make



Select double bond  from the Bond Order buttons and double-click on both **S–O** bonds. Be sure they have changed to double bonds.

4. Click the  button to do a quick molecular mechanics minimization of the energy.
5. Select **Setup, Calculations** from the menu. Choose *calculate*: **Equilibrium Geometry** *with* **Hartree-Fock, 6-31G***. *Total charge* should be **Neutral**, and *Unpaired Electrons* should be **0**. Select *compute:* **IR**. Click submit. Save the file when prompted and run the calculation.
6. From the **Summary** section of the **Output** (**Display** menu), record the energy of the molecule in your lab notebook. Record the frequencies of the SO_2 vibrations from the **Raman/IR Table** section of the Output Summary in your lab notebook.
7. Go to the **Display Spectra** area and view the calculated IR spectrum as you did for HCl and DCl. Animate the vibrations by highlighting the different frequencies. Assign frequencies as 'symmetric stretch', 'bend', or 'asymmetric stretch'.
8. Close the spectrum window.
9. Measure and record the **O–S–O** angle and the **S–O** bond length.
10. Return to the calculation setup window and repeat the HF calculation with a 3-21G basis set.
11. Submit the calculation. Record and compare your results for frequencies, bond length, and the angle with the previous calculation.
12. Repeat again using the **STO3G** basis set, the Semi-Empirical theories **PM3**, **RM1**, and **AM1,** and the Density Functional theory ωB97X-D with 6-31G* basis set. It might be a good idea to **Save as** each time to save each calculation in a separate file. Or if not, at least save a new file for each calculation model (HF, Semi-Empirical, Density Functional.

> **Note**
>
> If you do not save each calculation under a new filename, the new calculation overwrites the old in the current file.

13. Fill out the table of **Theories** and **Basis sets** for each combination.
14. Compare your results with your experimental (FTIR) data for SO_2 (CHEM 310 only), and literature data for frequencies, bond length and bond angle. Which combination of theory and basis set gives the most accurate prediction? Close your molecule.

Note

The NIST CCCBDB database is a good source for literature values for the SO_2 molecule (click here).

Table for SO_2	Theory	Basis set	S–O bond length(Å)	Bond Angle, (˚)	$nu1$	$nu2$	$nu3$
Ab initio	HF	STO-3G					
	HF	3-21G					
	HF	6-31G*					
Semi-empirical	PM3	N/A					
	RM1	N/A					
	AM1	N/A					
Density Functional	ωB97X-D, 6-31G*						
Your exptl. data							
Literature data*							
* Reference							

Note

This section of your lab notebook should include:

- A table that records, for each basis set:
  - Calculated energy of SO_2
  - Frequencies of SO_2 oscillations
    - Assign each frequency ‘symmetric stretch’, ‘bend’, or ‘asymmetric stretch’. You only have to do this for one basis set.
  - S-O bond length
  - O-S-O bond angle
- Comparison of calculated results to experimental (CHEM 310 only) and literature values
- Which combination of theory and basis set gives the most accurate prediction?

(See your ELN template for details)

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7.7: Exercise 4 - Modeling the Absorption Spectrum of Cyanine Dyes

This experiment is designed to build and study the series of conjugated dyes used in the UV-Vis experiment earlier in the course. For reference, the substitution number of napthalene is shown in the figure below (from Wikipedia).

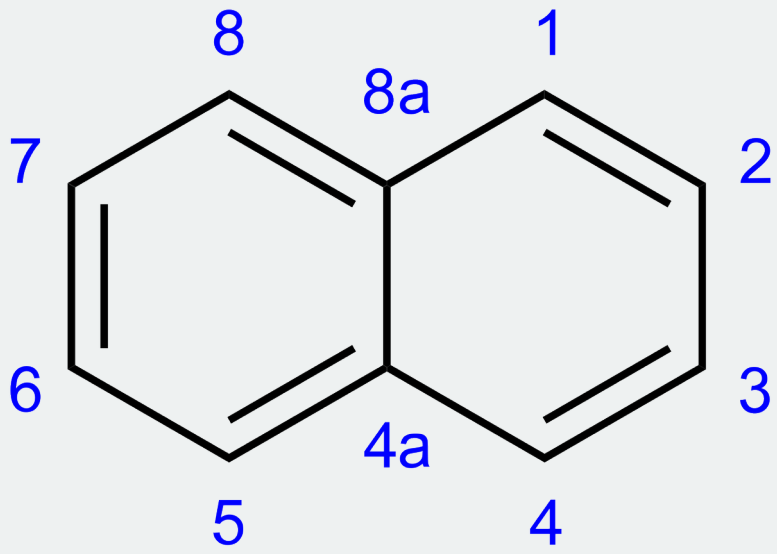
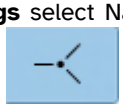


Figure 7.7.1: Numbering of the carbon atoms in naphthalene molecules according to latest (2013) IUPAC rules P-25.3.2.3 and P-25.3.3.1, which is the same as 1979 rule A-22. (By User:Edgar181 - Own work, Public Domain, https://commons.wikimedia.org/w/index...curid=22671537)

1. The first dye you will build and work with is the 1,1'-diethyl-4,4'-carbocyanine cation. (See Figure 3.2.2 in Experiment 1). Start a new file. Select the **Inorganic** tab of the Builder. Under **Rings** select N**aphthalene**. Click in the workspace to place a naphthalene ring on the screen. Now select the sp^2 hybridization  option and check to see that the element in the element selection button is Carbon. Move to the working area and add three sp^2 carbons to the 1-position of the naphthylene ring. At this point your structure should look something like this.

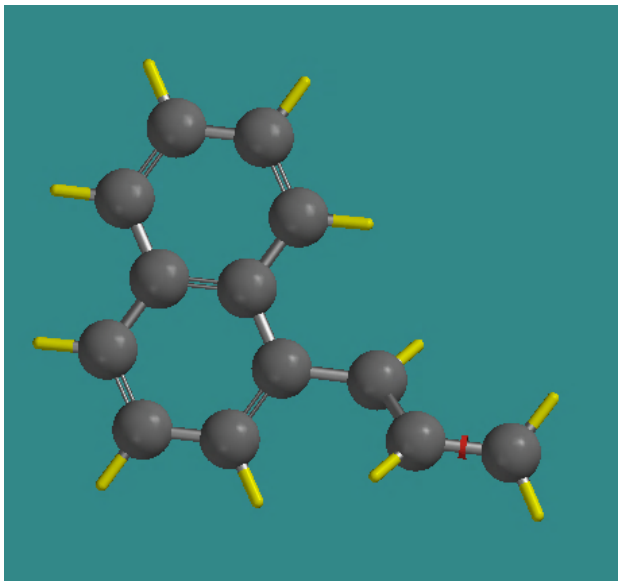
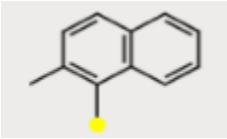


Figure 7.7.1: Adding sp^2 Carbons to the Naphthalene Ring. (CC-NC-BY-DUKE CHEM)

Return to the **Naphthalene** selection under **Rings** again. Notice the small yellow circle on the structure in the **Rings** window . This indicates the “active” valence of the naphthyl group. Make the 1-position of naphthyl active by clicking on the valence in the small structure window. Click on the free valence of the 3rd carbon atom in the working area, to add the second ring to your structure. At this point it might look something like this.

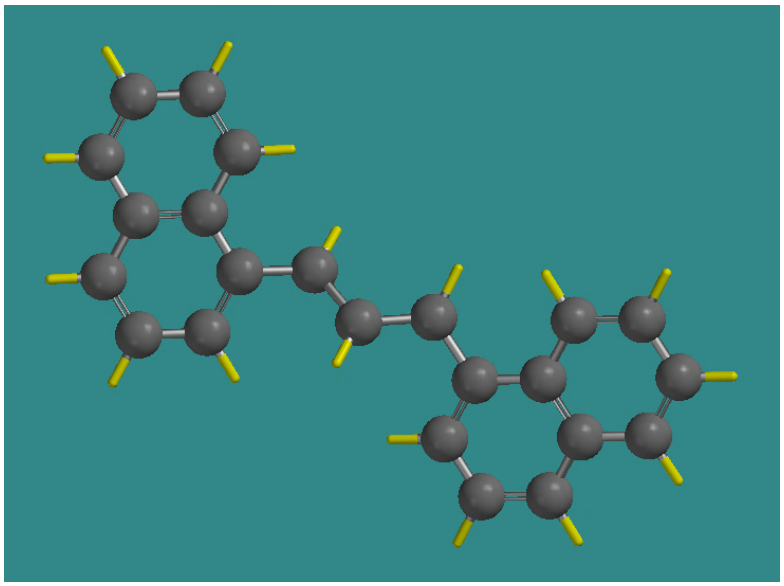


Figure 7.7.2: Adding the Second Naphthalene Ring. (CC-NC-BY-DUKE CHEM)

Now click on the delocalized bond . Double click on each C–C bond connecting the three carbons to each other and to the two rings. Look closely to be sure that all C–C bonds are delocalized.

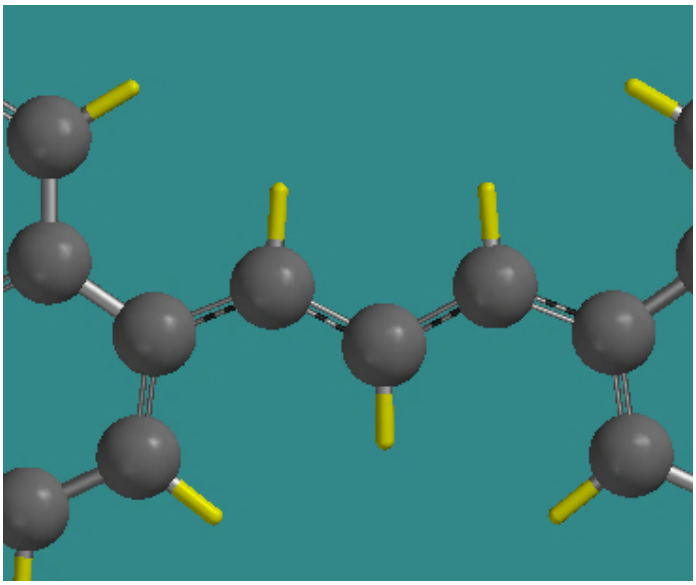


Figure 7.7.3: Changing the Bond Order of the Connecting Carbons. (CC-NC-BY-DUKE CHEM)

Click on the  button to minimize the structure. Chances are good that not all of the connecting carbons between the rings are in the trans- orientation, and that the overall structure is not yet planar. You can rotate around specific bonds to alter the conformation of the molecule. To do this, click on a bond you wish to rotate around. A red arrow appears, wrapping around the bond.

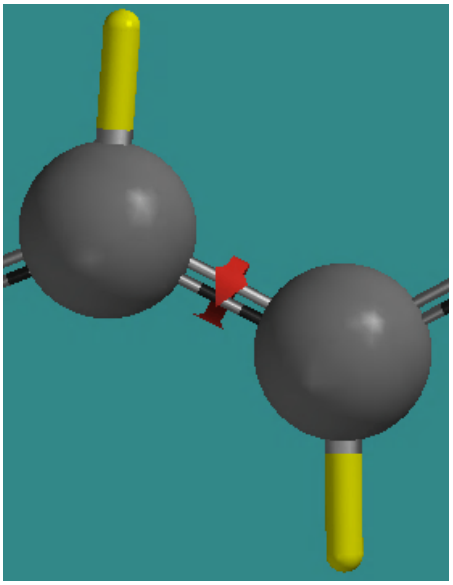


Figure 7.7.4: The Rotate Fragment Arrow. (CC-NC-BY-DUKE CHEM)

Hold down both the control and shift keys and click and drag the left mouse button to rotate a fragment of the molecule around the selected bond. In this way put all of the connecting carbons into the trans-orientation, and position the rings so that they point up and outward away from each other. Click again on the  button to minimize the structure. It should now be planar and look like this.

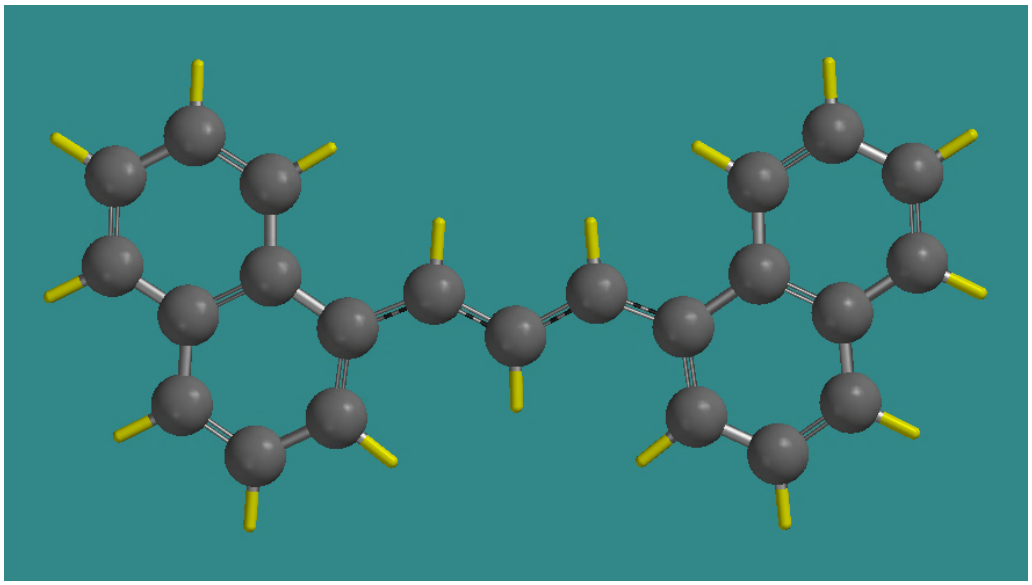


Figure 7.7.5: The Nearly Completed Structure. (CC-NC-BY-DUKE CHEM)

Return to the element section button and choose Nitrogen. Double-click on the carbon atoms of the naphthalene rings that are para- (across from, and in position 4) to the connecting three-carbon chain (look ahead to Figure 7.7.6). The color of the atom should change to blue as the element changes from carbon to nitrogen. Change the element selection button back to Carbon, and change the hybridization to sp^3 . Add ethyl groups to the free valence of the nitrogen atoms. **Minimize** the structure using . Check your structure. Is it planar? The final molecule should look something like this (rotated some to show the planar nature).

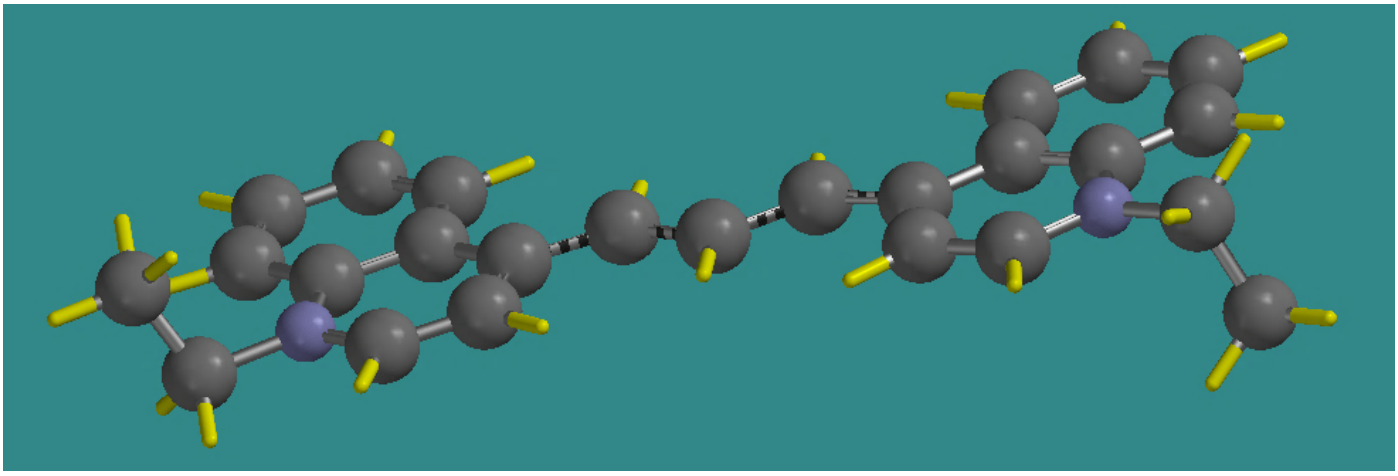


Figure 7.7.6: The Completed Structure. (CC-NC-BY-DUKE CHEM)

Notice in this picture that the ethyl groups are positioned axial to the plane of the rings. **Save** this molecule as dye4.

2. At this point you might see that it take more work to build a larger molecule. It might be prudent, therefore to keep the dye4 file safe, just in case something happens and you need to recall it. To do so, select **Save as** from the **File** menu and save the file as **dye4_MNDO.** Select **Setup, Calculations** from the menu. Choose *calculate*: **Equilibrium Geometry** *at* **Ground State** *in* **Gas** *with* **Semi-Empirical, MNDO**. Set *Total charge* : **Cation**, *Unpaired Electrons*: **0**. Click **Submit**.

3. Once the calculation is finished, inspect the molecule. Did the conformation change? Inspect the **Output** and record the

equilibrium geometry **Energy** from the **Summary** section in your lab notebook.

4. In preparation for the next calculation select **Save As** from the **File** menu and name the file **dye4-ci.** Then select **Setup**, **Calculations** again, and change the parameters to, *Calculate*: **Energy** *at* **Ground State** *in* **Gas** *with* **Semi-Empirical, MNDO**. Set *Total charge* : **Cation**, *Unpaired Electrons*: **0**. In the *Options* box: type **CI PRINTLEV=2**. Click **OK**.

Make sure the above is correctly entered: note Energy instead of Equilibrium Geomentry

5. **Submit** the calculation.

6. Inspect the **Output** when the calculation is finished. From the **Output** tab, look for the table of **Spin Allowed Singlet Excitations** (immediately below the very long list of Slater Determinants) find the wavelength (in nm) and energy (in eV) of the first transition (it should have a large oscillator strength, OS). Record these values in your lab notebook.

7. Compare your computational results with your experimental and theoretical data generated in the previous "wet lab" dye experiment. Repeat steps 2-6 on dye4 using **AM1** and **PM3** models.

Dye 4	E, kcal/mol (from the Equilibrium Geometry calculation)	Energy of transition (eV)	λ_{max} (nm)
MNDO			
AM1			
PM3			
For Comparison: λ_{max} from Expt 1 =			

Things to Think About

- **A Change in Conformation Leads to a Change in Calculated λ_{max}:** You might have noticed during Exercise 3 with SO_2 that with each change in calculation theory (HF, Semi-Empirical, Density Functional) and with each basis set within a given theory, the calculated bond lengths, bond angles, and frequencies of vibration changed. In the same way in this current exercise with the dyes, if you look closely you will see that changing the approximations within the Semi-Empirical calculation (MNDO, PM3, AM1) each lead to slightly different conformations of the molecule. As the result, the predicted value of both the Energy and λ_{max} changes.
- **Seeing Trends in the Calculated Results, and that λ_{max} Changes with Conformation is Likely More Important than Seeing if the Calculation Gave the "Right" λ_{max}:** It would be nice if your calculation could give a calculated λ_{max} in complete agreement with what you saw for the dye when you did the UV-Vis spectrum in Experiment 1. But thinking about it, there are good reasons why it would not be expected to. For one, your calculation is for a single molecule in the gas phase. In Experiment 1 you measured the spectrum of a large number of molecules in solution in methanol. Indeed, one would expect the results to be different. Does that mean that the calculation is of little value?
- **Thinking about This**: Explain why the actual UV-Vis spectrum of the dye in Experiment 1 had such broad peaks. (Perhaps this understanding, coming from the results of these calculations, is more important than seeing if the calculation gave the "right" λ_{max}.)

8. Look over the results from Dye 4. Which semi-empirical calculation (MNDO, AM1 or PM3) gave the best result when comparing λ_{max} to your Experiment 1 result? Build the other three dyes. Perform that same semi-empirical calculation for each. Determine the energy of the equilibrium geometry, and the energy (in eV) and λ_{max} of the spin allowed singlet excitation. Record the results.

Semi-empirical Calculation did you used					
	Name	Equil. Geom. E, (kcal/mol)	Energy of transition (eV)	Calc. λ_{max} (nm)	Exptl. λ_{max} from Expt. 1
Dye 1	1,1'-diethyl-2,2'-cyanine				
Dye 2	1,1'-diethyl-2,2'-carbocyanine				
Dye 3	1,1'-diethyl-2,2'-dicarbocyanine				
Dye 4	1,1'-diethyl-4,4'-carbocyanine				

9. What can you conclude at the end of this exercise? Do you see the expected trend in λ_{max} as a function of the conjugation length of the connecting carbons between the cyanine rings? Does this more sophisticated calculation give more accurate results in terms of predicting λ_{max} for the series of dyes as compared to the theoretical, model-based values you calculated in the first dye experiment? Looking only at Dye 4, which you might recall from Experiment 1 did not show the expected increase in λ_{max} even though the conjugation length was greater than Dye 3, did the semi-empirical calculation do a better job of accurately predicting the change in λ_{max} as you move from Dye 3 to Dye 4?

Note

This section of your lab notebook should include:

- A table recording, for each dye:
  - Equilibrium geometry energy
  - Energy of the first spin-allowed singlet transition
  - Wavelength of the first spin-allowed singlet transition
- Comparison of computational λ_{max} to experimental λ_{max} and theoretical λ_{max} from the previous dye experiment
- Which semi-empirical calculation gave the most accurate result?
- Do you see the expected trend in λ_{max} as a function of the conjugation length of the connecting carbons between the cyanine rings?
- Does this more sophisticated calculation give more accurate results in terms of predicting λ_{max} for the series of dyes as compared to the theoretical, model-based values you calculated in the first dye experiment?
- Looking only at Dye 4, which you might recall from Experiment 1 did not show the expected increase in λ_{max} even though the conjugation length was greater than Dye 3, did the semi-empirical calculation do a better job of accurately predicting the change in λ_{max} as you move from Dye 3 to Dye 4?

(See your ELN template for details)

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7.8: Exercise 5 - Modeling an Intramolecular Rearrangement

This exercise is designed to calculate the transition state of the thermal conversion of vinyl alcohol to acetaldehyde using a semi-empirical calculation method. Along the way it will show you how you can model a chemical reaction (in this case an intramolecular rearrangement), and using spreadsheet functionality and graphing to create a reaction profile.

1. Start a new file. Build vinyl alcohol. In the Organic tab, use  to construct the carbon skeleton. Select the  oxygen and click on one of the free valences on the vinyl skeleton. If needed rotate the CO bond into the cis-configuration (i.e., bringing the alcohol hydrogen into position over the C=C double bond). Minimize the structure using .

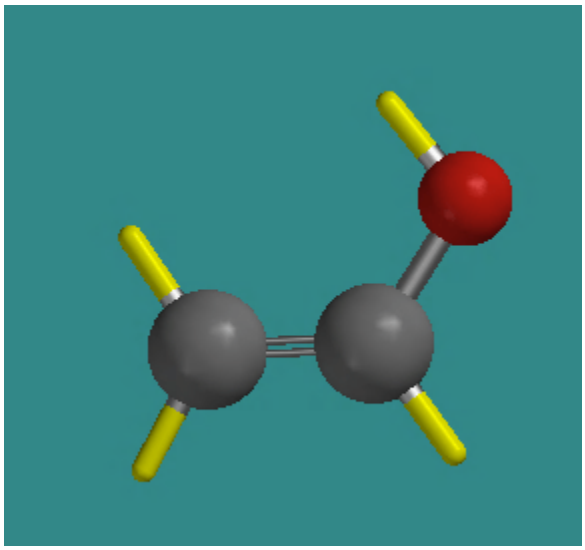


Figure 7.8.1: Vinyl Alcohol. (CC-NC-BY-DUKE CHEM)

2. Setup the following calculation: **Equilibrium Geometry** *from* **Ground State** *in* **Water**, *with* **Semi-Empirical, AM1**. *Total charge*: **Neutral**, *Unpaired Electrons* : **0**. Click **Submit**. Save the file as vinyl alcohol, and let the calculation run
3. When it has finished, go the Summary tab of the Output and record the **Energy** in kJ/mol in your lab notebook.
4. Select **Save As** from the File menu and create a copy of this molecule under the name, **vinyl alcohol_ts**. Select **Guess Transition State** from the **Build** menu.
5. Click on the C=C bond and then the C-O bond. Next, click on the O-H bond and, while holding down the SHIFT key, click on the O-H hydrogen to be transferred and then on the carbon atom to receive this hydrogen. Another electron-pushing arrow should appear along with a faint blue dotted line between the O-H hydrogen and the carbon. It should look like this.

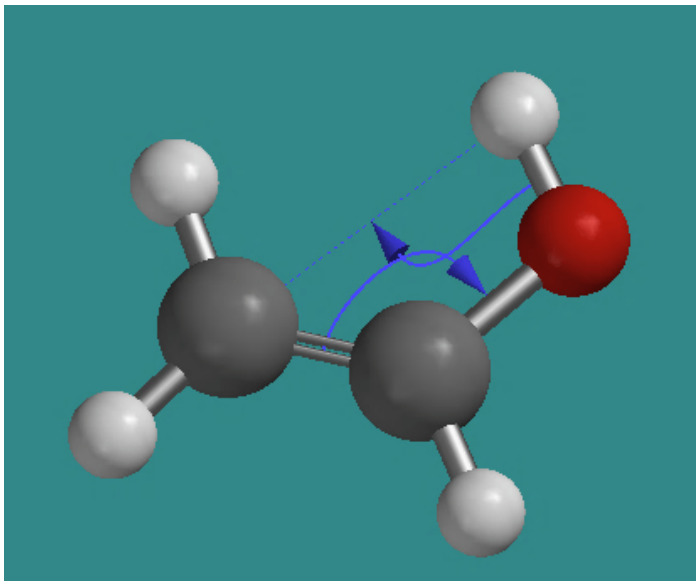


Figure 7.8.2: Building the Transition State Query. (CC-NC-BY-DUKE CHEM)

6. Click on the  button at the lower right of the screen. In a few seconds your initial structure will be replaced by a calculated transition state structure. There should be a name (1_3-H-Shift_ethenol_AM1.ts (Exact)) at the lower right corner of the screen, and the structure should look like this.

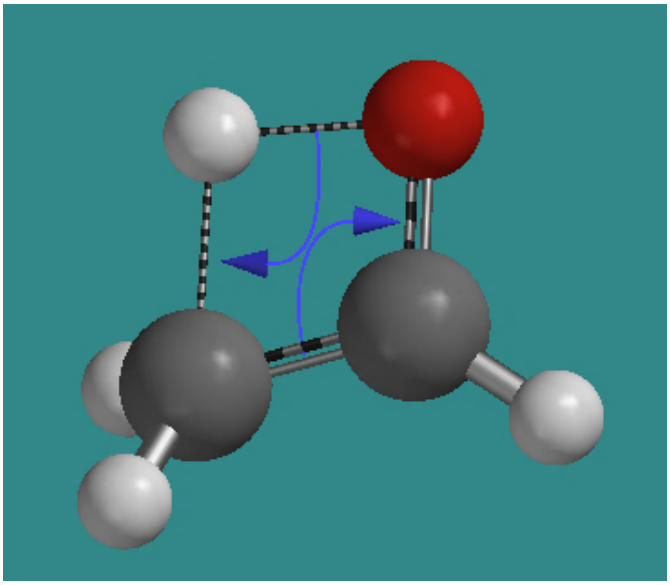


Figure 7.8.3: The Guessed Transition State. (CC-NC-BY-DUKE CHEM)

7. Setup the following calculation: *Calculate* **Transition State Geometry** with **Semi-empirical** *with* **AM1** *in* **Water.** *Charge* should be **Neutral**; *Unpaired Electrons*, **0**; *compute*: **IR. Submit** the job.
8. When it has finished, examine the geometry of the transition state using the **Geometry** functions (bond lengths and angles). Go to **Display, Output** and record the energy of the transition state structure.
9. Select Spectra under the Display menu. Use the  and  to display the calculated IR and frequency table.

Animate the vibrational mode corresponding to the “imaginary” (i) frequency. You might click the  button and change the Steps to 30 to slow down the animation.

The Imaginary (i) Vibration

The idea is this: By now I am sure you are familiar with a potential energy well showing how the energy of a bond varies as a function of internuclear distance. The minimum of this well represents the equilibrium bond length. Additionally, you know that the tie-lines across this potential well represent vibrational modes of the bond. Now a similar tie line across the potential energy curve of a reaction profile, near where the maximum in the curve represents the transition state of the molecule. We can imagine, and calculate a value for, such a vibrational mode associated with this idea. This calculated "imaginary" vibration is typically denoted with an i, and models the dynamics of the molecule as it traverses over the top of the activation energy barrier through the transition state structure.

Notice in the animation that the C=C double bond lengthens as the hydrogen moves toward the carbon, and that the carbon accepting this hydrogen shifts from sp^2 toward sp^3 geometry. Notice also that the C-O bond shortens with the hydride shift as it starts to become a C=O bond. And also that the forming carbonyl carbon shows the shift from sp^3 to sp^2 geometry. That is, this one calculated imaginary vibration shows the structural changes in the transition state and across the top of the activation energy barrier in a reaction profile. Stop the animation and close the Spectrum window.

10. Build acetaldehyde as a **New** file. Set up the same **Equilibrium Geometry** calculation as you did for vinyl alcohol (**Semi-empirical, AM1, Water**). Save the file and **Submit** the calculation. Record the energy as you did for vinyl alcohol and the transition state. Close your molecule.

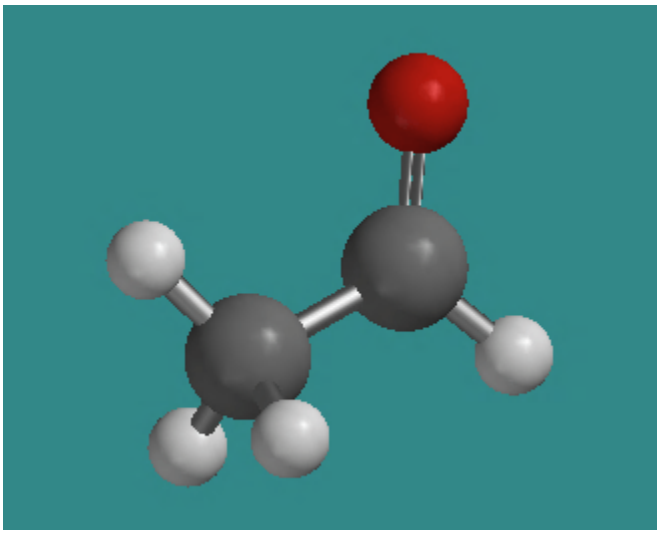


Figure 7.8.4: Acetaldehyde. (CC-NC-BY-DUKE CHEM)

Creating the Reaction Profile:

11. Open your vinyl alcohol molecule made and optimized in steps 4.8.1-4.8.2. From the **File** menu, select **Save-as** and save the file as Reaction Profile. Select **Spreadsheet** from the **Display** menu. A spreadsheet appears on the screen with one entry. This entry is your vinyl alcohol molecule. Double-click on the M001 entry and change the name to Vinyl Alcohol.

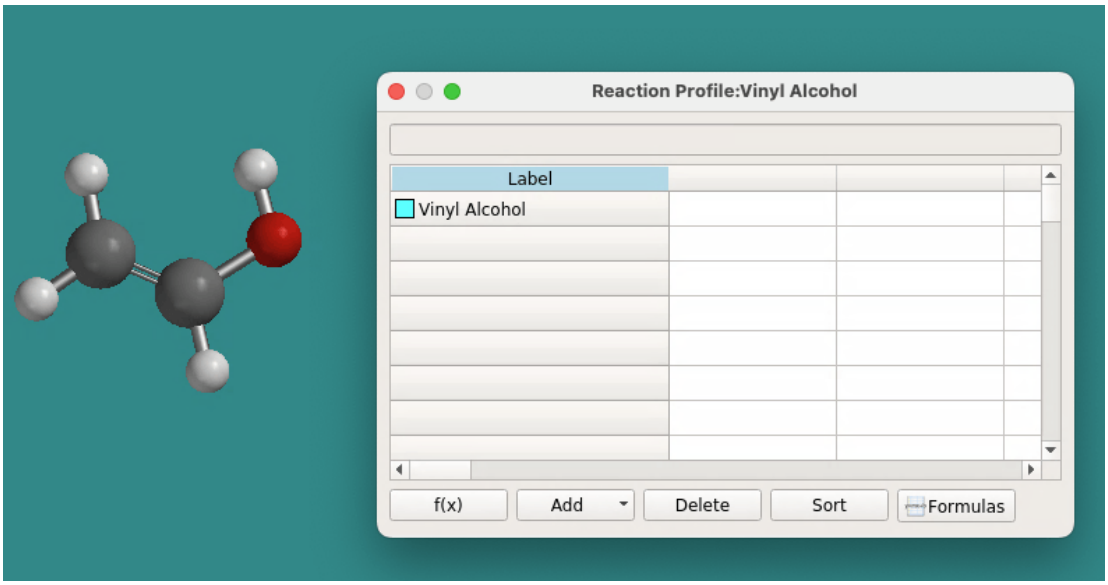


Figure 7.8.5: Adding Molecules to a Spreasheet. (CC-NC-BY-DUKE CHEM)

12. Now open the transition state molecule created and optimized in steps 4.8.4-4.8.7 above. Notice that this molecule opens in its own window (you can see the tabs at the lower left of the Spartan screen). Use **Select All** from the **File** menu to highlight the molecule (or right click on the molecule and select all). Use **Copy** from the **File** menu (or right mouse click – **Copy**) to copy the molecule to the Spartan clipboard. Return to the vinyl alcohol/spreadsheet screen by clicking on its tab. Click once on the cell immediately under the vinyl alcohol entry. Right-click *on that same cell* and paste the transition state into the spreadsheet. Change the name to Transition State.
13. Open and paste your acetaldehyde molecule into the third spreadsheet cell. At this point your spreadsheet will look like this.

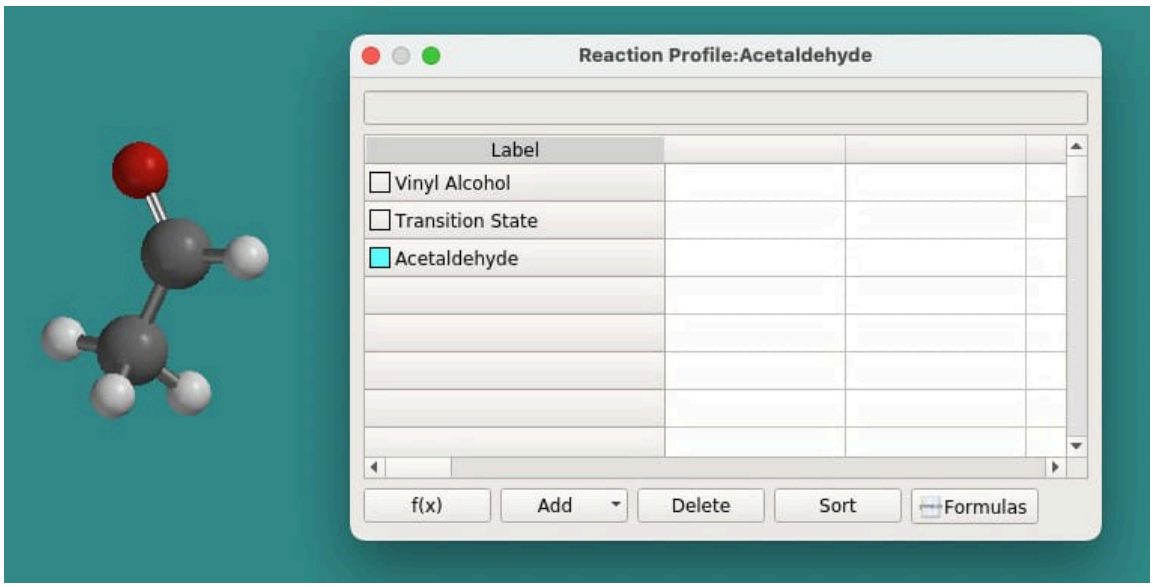


Figure 7.8.6: The Three Molecules in the Spreadsheet. (CC-NC-BY-DUKE CHEM)

14. Open the **Setup Calculations** box for each of the three molecules in the spreadsheet and confirm that the desired calculation is correct for each. If it is not, correct them. It should be Equilibrium Geometry in water, with semi-empirical, AM1 for vinyl alcohol and acetaldehyde; and, Transition State Geometry in water with AM1 for transition state molecule. Click **OK** (not Submit) to close the Setup Calculations box each time.
15. Click the **Add** button in the spreadsheet window. Select **Energy (kJ/mol)** from the list of choices. Click **OK**. You will notice a new Energy column appear in the spreadsheet, with Pending next to each molecule.
16. Return to the **Setup Calculations** box. Click **Submit**. The calculations will run and when complete the spreadsheet will show the aqueous energies for all three entries.

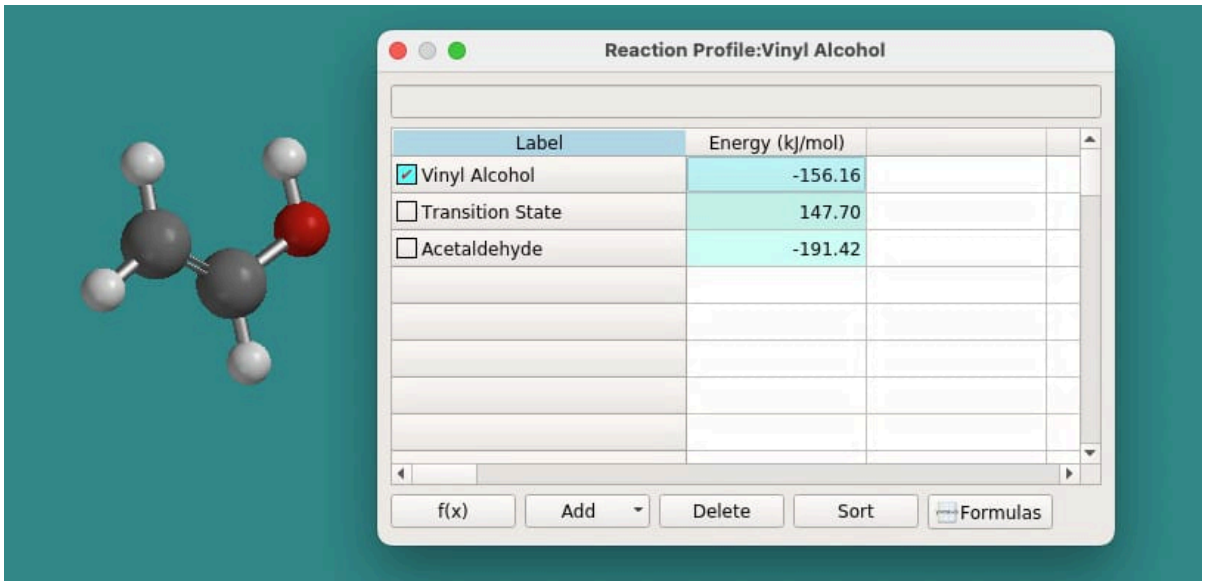


Figure 7.8.7: The Completed Calculations. (CC-NC-BY-DUKE CHEM)

17. Select Plots from the Display menu. Click on the  button and highlight Energy in the window that appears. Click Create. A plot appears in a window to the right of the molecule screen. Click  and select Smooth from the Curve options. Add a Title, and click Done. Click , and the plot, showing the reaction profile (Energy vs molecule) will move to the main screen. You can use the Animation bar, , to step through the profile, showing the structure at each point in the process. Record images of the reaction profile in your lab notebook. Use the energy values from the spreadsheet to calculate the activation energy and ΔH for the reaction.

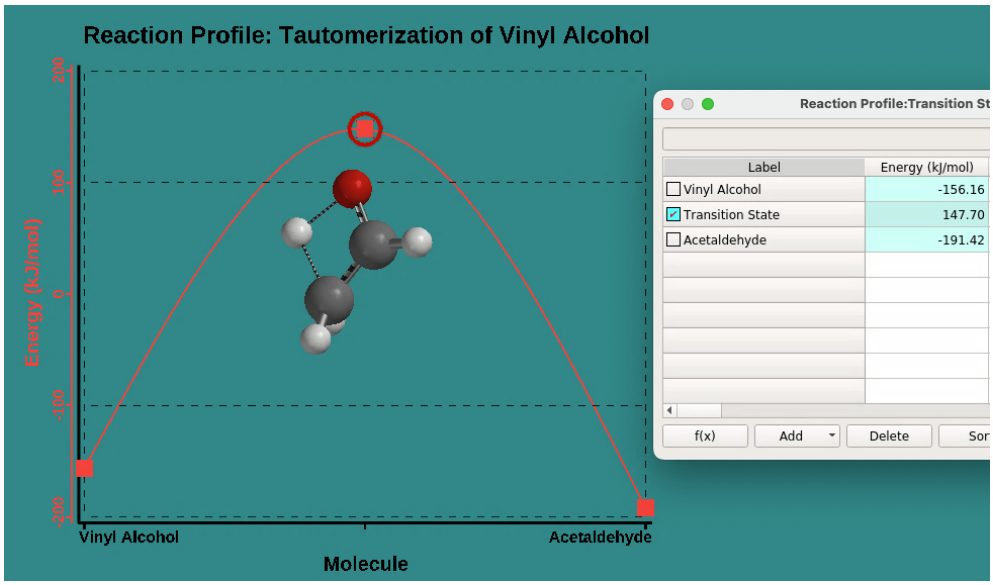


Figure 7.8.8: The Reaction Profile. (CC-NC-BY-DUKE CHEM)

Note

This section of your lab notebook should include:

- The equilibrium geometries energies of the initial, transition, and final states
- Images of all reaction profile plots
- Calculation of the activation energy and ΔH of the tautomerization reaction

(See your ELN template for details)

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8: INDEPENDENT PROJECT

8.1: Pre-Lab and Introduction
8.2: Literature
8.3: Computational

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8.1: Pre-Lab and Introduction

Pre-meeting assignment for Independent Project

Prior to the first scheduled meeting for the Independent Project, do the following:

- Complete the Electronic Structure Calcuations from the previous module.
- Read this entire module.
- Submit two ideas for a project topic to Canvas. Your two proposals can be for either two computational project ideas, two literature project ideas, or one of each. These do not need to be the project you end up with, but you do need to start thinking about what questions you want to ask and answer.

This project is only assigned to students in CHEM310L (not CHEM301L). Its time to see how physical chemistry can be applied to a topic that really interests you.

In 310L, you can choose a topic for your independent project, and choose whether you would like to dive into more computational work, or explore other applications of physical chemistry in the peer-reviewed literature. You should begin searching the literature (eg using Web of Science or looking at the Table of Contents for leading Physical Chemistry journals) for physical chemistry topics that interest you. Alternatively, you can think about simple chemical phenomena or reactions that you are interested in and that you can model using Spartan. You should prepar a brief written proposal (1 paragraph) on at least two ideas for what you might do for your independent project and be prepared to discuss it with your instructors.

You will choose a topic, study it using computation or literature, and present your work to your classmates. Please prepare two proposals for this project and discuss them with your instructors.

Objectives of the Independent Project:

1. To apply what you're learned in class and lab to learn more about computation and/or a cutting edge research application!
2. To teach your classmates about a cool new topic in physical chemistry!
3. To practice communicating technical scientific topics through an oral presentation.

Project options

You may choose from one of the following options for your independent project:

1. Literature Project: Read a research article and present it as an application of physical chemistry.
2. Computational Project: Design a mini research project using electronic structure calculations, and present your results and conclusions.

Final Presentation

Your learning during this project will be demonstrated through a short in-class presentation. You will present the findings of your project to the class in a 7-minute presentation on the scheduled presentation day (see syllabus schedule). You will be graded on the information you present and your ability to answer any questions from your peers. If you have questions about format, ask us!

Peer Review

During the presentations, you will peer review your classmates. You will be assessed on your critical review of other students' works, and your feedback will be shared with those students anonymously. However, your review will not determine other student's

grades.

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8.2: Literature

One option for your independent project is to explore a topic from class (lab or lecture) that intrigues you and find its application in modern chemical literature. This option would allow you to familiarize yourself with prominent physical chemistry journals, search chemical literature, and apply class concepts to real world applications.

This will involve looking at physical chemistry journals, choosing an article, reading the article critically, and summarizing the contents for your peers. The article you choose must a **full research article** (not a communication or a review article) and has been published recently (in the last **5 years**) in a reputable **physical chemistry journal**.

Find an article:

Start by seeing what's out there. Find the table of contents for a journal that focuses on physical chemistry or find the most popular articles for the last 12 months from one of the ACS journals. Links for some of the Journals of Physical Chemistry from ACS are linked below.

- Journal of Physical Chemistry A
  - Current Issue (https://pubs.acs.org/toc/jpcafh/current)
  - Top articels (https://pubs.acs.org/action/showMost...nalCode=jpcafh)
- Journal of Physical Chemistry B
  - Current Issue (https://pubs.acs.org/toc/jpcbfk/current)
  - Top articles (https://pubs.acs.org/action/showMost...nalCode=jpcbfk)
- Journal of Physical Chemistry C
  - Current Issue (https://pubs.acs.org/toc/jpccck/current)
  - Top articles (https://pubs.acs.org/action/showMost...nalCode=jpccck)
- The Journal of Physical Chemistry Letters
  - Current Issue (https://pubs.acs.org/toc/jpclcd/current)
  - Top articels (https://pubs.acs.org/action/showMost...nalCode=jpclcd)

With one of the lists, do the following.

1. Spend 10 minutes to scan the titles and abstracts of the articles in the latest issue(s).
   a. What subdisciplines or applications of physical chemistry do you notice?
   b. Are there any applications that surprise you?
   c. Is there anything that piques your interest?
2. Look at the synopsis figure that accompanies each title.
   1. Do the figures change your assignment of subdiscipline?
   2. Do the figures change your interest in reading the article?
3. Choose one paper that you would be interesting in learning more about and examine the abstract more closely. Decide if you want to actually read this paper. If not, move on to another, check out the Journal's ASAP articles, or go to a different journal to find something that is interesting to you. Alternatively, you can check out the list of top articles read for a specific year (eg: Top articles for 2021 are here: https://axial.acs.org/2022/01/20/mos...articles-2021/)

Structure your presentation

You will present the published research as if you were a researcher in the group of authors. You do not need to present the entire paper with all of its data. Select one or more of the most important points (the most important pieces of data, and conclusions drawn from them) from the paper and let that be the topic of your presentation.

In structuring your presentation:

1. Start is with the **question** the authors sought to answer. Give enough background about the question so that your audience can understand why the question is interesting or important.
2. Describe the **methods** used to answer the question. You do not need to cover each method in depth, but give your audience

enough information that they can understand the meaning of the data you present.
3. Describe the **results**. As with the methods, help your audience understand what each piece of data means, but be concise.
4. Describe what **conclusions** were made from these results. Your audience should be able to understand how the results add up to the **conclusion** that were drawn.
5. Finally, you can bring up any limitations, changes you would make to the study, outstanding questions, and new directions.

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8.3: Computational

First, gain familiarity with electronic structure calculations in the previous module!

If you have lingering questions from a class or from your individual research that might be addressed using electronic structure calcuations, you can try to do so in this project! Once the Electronic Structure Calculations module is complete, you will have an understanding of the software's capabilities. Talk to your instructors about ideas or submit a proposal on Gradescope.

Examples of previous student's projects:

- Using Spartan to model tautomers of fluorescein to determine if absorption spectra would differ.
- Modeling a reaction mechanism to determine the energy of a transition state which would help explain confusing experimental results.
- Looking at the relative energies of ozone formation and ozone's reaction with oxygen and ozone depleting molecules.

Structure your presentation

One way you could structure your presentation is as follows.

1. Start with the **question** you sought to answer. Give enough background about the question so that your audience can understand why the question is interesting or important.
2. Describe the **methods** you used to answer the question.
3. Describe your **results**.
4. Describe the **conclusions** you make from the results. Your audience should be able to understand how your results add up to the **conclusion** you have drawn.
5. Finally, you can bring up any limitations, changes you would make to the study, outstanding questions, and new directions.

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9: HOW SHOULD APPLES BE PREPARED FOR A FRUIT SALAD?

Learning Objectives

Process Learning Objectives:
At the end of this experiment, you will be able to ...

1. Analyze and manipulate equations and graphical representations to appropriately model experimental data/results.
   a. Fit a nonlinear function to data.
   b. Convert a nonlinear relationship to a linear form.
   c. Extract relevant information from the results (i.e. slope, intercept, coefficients).
2. Choose experimental conditions to obtain appropriate data for analysis.

Content Learning Objectives
At the end of this experiment, you will be able to ...

3. Describe the Michaelis-Menten mechanism for enzyme catalysis, including the meaning of the Michaelis-Menten parameters.
4. Determine which apple has the slowest rate of browning, making it the best choice for a fruit salad.
5. Identify chemical inhibitors of the PPO enzyme and distinguish a true enzyme inhibitor from other actions or factors that inhibit browning of apples.

9.1: Pre-Lab Assignments

9.2: Introduction

9.3: Part I, The effect of apple extract on oxidation of catechol

9.4: Part II, Does the type of apple matter?

9.5: Part III, Inhibition of catechol oxidation

9.6: Part IV, thermal stability of catalase (under construction)

9.7: Experimental Procedure for Parts I - III

9.8: Post-Lab

9.9: References

This experiment is adapted from Cole, Renée S., Marc Muniz, Erica Harvey, Robert Sweeney, and Sally Hunnicutt. “How Should Apples Be Prepared for a Fruit Salad? A Guided Inquiry Physical Chemistry Experiment.” *Journal of Chemical Education* 97, no. 12 (December 8, 2020): 4475–81. https://doi.org/10.1021/acs.jchemed.0c00517.

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9.1: Pre-Lab Assignments

📅 **Due:** Each pre-lab assignment must be completed before 1:00 PM on each scheduled lab meeting day (see syllabus schedule).

- **Part I is due prior to the first Wet Lab meeting (see syllabus agenda)**.
- **Part II is due prior to the Wet Lab meeting (see syllabus agenda).**

🕒 **Time:** Plan at least two hours to complete each pre-lab assignment below (2 hours each week).

🎯 **Purpose**: These pre-meeting assignments are designed to help you arrive to each week's meeting prepared to engage in thoughtful discussion and to conduct the experimental work.

This module has two "parts" that include **Wet Lab** work (Part I and Part II). In addition, there are planning activities that precede the experimental work, but are not described here (see Canvas and your syllabus agenda). You should prepare for both Wet Lab meetings by dressing appropriately for lab and bringing your own safety eyewear. Wear PPE and gloves when handling hazardous materials.

Pre-Lab assignments

Read this entire module. Each experimental "part" (Part I and Part II) will be completed on a different day. Please complete the appropriate written assignment for each date (to be turned in on Canvas/Gradescope). Each assignment is described below, and is described on the pages for Part I and Part II.

Pre-Lab Assignment for Part I: Which Apples are Best?

9.3: Part I, The effect of apple extract on oxidation of catechol

9.5: Part III, Inhibition of catechol oxidation

Adapted from Cole, Renée S., Marc Muniz, Erica Harvey, Robert Sweeney, and Sally Hunnicutt. “How Should Apples Be Prepared for a Fruit Salad? A Guided Inquiry Physical Chemistry Experiment.” Journal of Chemical Education 97, no. 12 (December 8, 2020): 4475–81. https://doi.org/10.1021/acs.jchemed.0c00517.

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9.2: Introduction

Many fruits and vegetables contain phenolic compounds, which play an important role in the flavor and color of the fruit. The oxidation of phenols into quinones, which polymerize into brown products, results in the browning of fruits and vegetables.[1,2] However, most foods, such as bananas, potatoes, and apples, only produce significant amounts of quinones when they are exposed to the O_2 in air after they have been cut or bruised. When the fruit is cut and cellular compartmentalization is disrupted, these compounds can be involved in both enzymatic and non-enzymatic browning reactions.[1,3] Catecholase, also known as catechol oxidase or tyrosinase, is an enzyme found in many plants, animals, and fungi. The general function of catecholase is to accelerate the reaction between oxygen and phenolic compounds to produce quinones and water.[3-5] Enzyme activity and susceptibility to browning have been shown to have varietal dependence[2,6] in addition to differences among different types of fruit.

The production of quinones from the phenolic compounds is significant because quinones are part of a class of toxicological intermediates that can create a variety of hazardous effects.[7,8] Quinones can be converted to semiquinone radicals, which can either directly interact with DNA or may interact with molecular oxygen to produce genotoxic reactive oxygen species that can cause oxidative stress and DNA damage.[7-9] Many bacterial strains are very sensitive to the genotoxicity of oxidative stress[9,10], so the production of quinones provides some anti-bacterial protection to the fruit. Unfortunately, it also results in unpleasant tastes and textures, which is a concern when preparing fruits for human consumption.

The reaction we will study to address the question in the title of the experiment is the catalyzed oxidation of catechol by molecular oxygen to form 1,2-benzoquinone and water. Quinone is the only species in the reaction mixture that absorbs light in the visible region.

References

1. Rocha, A., & Morais, A. M. "Polyphenoloxidase activity and total phenolic content as related to browning of minimally processed 'Jonagored'apple." *J of the Science of Food and Agriculture*, **2002**, *82*, 120-126.
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7. Bolton, J. L., Trush, M. A., Penning, T. M., Dryhurst, G., & Monks, T. J. "Role of quinones in toxicology," *Chemical research in toxicology*, **2000**, *13*, 135-160.
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10. Hakura, A., Mochida, H., Tsutsui, Y., & Yamatsu, K., "Mutagenicity of benzoquinones for Ames Salmonella tester strains," *Mutation Research Letters*, **1995,** *347*, 37-43.

Adapted from Cole, Renée S., Marc Muniz, Erica Harvey, Robert Sweeney, and Sally Hunnicutt. "How Should Apples Be Prepared for a Fruit Salad? A Guided Inquiry Physical Chemistry Experiment." *Journal of Chemical Education* 97, no. 12 (December 8, 2020): 4475–81. https://doi.org/10.1021/acs.jchemed.0c00517.

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9.3: Part I, The effect of apple extract on oxidation of catechol

Pre-lab assignment for Part I: Does apple extract catalyze oxidation of catechol?

📅 **Due before Wet Lab Meeting for Part I**

Read sections 9.3 and 9.7 of this manual and complete the GENERAL PRE-LAB ASSIGNMENT for this part of the module. Then complete the following written assignment and submit your work before the deadline. Do not use AI/LLMs to complete any part of this assignment.

Files to support this experiment are here (click).

1. **Monitoring the catechol oxidation reaction:**
   a. Look up the formulas and structures of catechol and 1,2-benzoquinone ("quinone"). Write the balanced chemical equation for the oxidation of catechol to quinone. Using ChemDraw, create a figure showing the balanced equation with skeletal structures of the organic reactant and product. Embed your figure in the Google Doc template for this assignment, and attach the chem draw file you created in your pre-lab submission in Google Classroom.
   b. Examine the functional groups and structural properties of the reactant and product. Suggest an accessible experimental method for monitoring the progress of this reaction, and explain your reasoning.
   c. Based on your suggested experimental method, what data will be collected, and how will you determine the initial rate of reaction from this data?
2. **The Model:**
   a. Briefly define an enzyme and describe in general terms how enzymes affect reaction rates.
   b. Enzyme catalyzed reactions typically follow the "Michaelis-Menten mechanism," which may be represented by

$$\mathrm{E} + \mathrm{S} \rightleftarrows [\mathrm{ES}] \rightarrow \mathrm{E} + \mathrm{P} \tag{9.3.1}$$

   Define E, S, and P for this mechanism in terms of the catechol reaction in question 1.
3. Read through the protocol. In your lab notebook before class, propose a specific plan for the following steps. You will need to use knowledge from pre-requisite courses to complete the plan. When writing your plan, be specific. Consider the volume of solution needed for the number of people doing the experiment.
   a. Write a plan for creating the buffer.
   b. Write a plan to extract the juice from the apple puree.
   c. Write a plan for creating the two stock catechol solutions.
   d. What liquid should be used for the reference spectrum (the "blank")?
   e. Describe the procedure used to obtain the designated amount of each component in the reaction mixture. Explain why the solutions are added in a specified order.
4. **Predict Results:**
   By hand, sketch a curve showing the expected absorbance versus time graph for a solution containing catechol and enzyme. Label the axes. Explain your prediction.
5. **Create a table** in your lab notebook that approximately follows the format below. An example of an electronic version of a table is here (click). Fill in as much of the table as you can using the information in the procedure below.

Run#	File name	Comment	Volume of Enzyme	Volume of Substrate	Volume of Buffer or Water
Run 1	YYYYMMMMDD_AppleVariety_Run1	Part 1A, Catechol only			
Run 2	YYYYMMMMDD_AppleVariety_Run2	Part 1A, Catechol + Enzyme			

Run#	File name	Comment	Volume of Enzyme	Volume of Substrate	Volume of Buffer or Water
Run 3	YYYYMMMMDD_AppleVariety_Run3	Part 1A Catechol + E + Buffer			
Run 4	YYYYMMMMDD_AppleVariety_Run4	Part IIA			
Run 5		Part IIA			

(add more rows as necessary...)

Procedure

The experimental conditions are described below. The detailed procedure for obtaining appropriate materials, operating the UV-vis instrument, and conducting the experiments is found here: Protocol (click here). For Part I, each group will select one type/variety of apple to use in these experiments. Then the entire class will share data

Part I Experiment: How does apple extract effect oxidation of catechol? Does pH matter?

How does enzyme extracted from an apple affect the rate of oxidation of catechol, and how does buffering affect the rate? Select an apple varietal (for example, Granny Smith, McIntosh, Pink Lady...). Compare the oxidation of catechol under three conditions: no added apple juice, with added buffered apple juice, and with unbuffered apple juice of the same variety.

1. **Run 1:** For reaction mixture 1, mix 2.0 ml of catechol in water with 0.5 ml of water.
2. **Run 2:** For reaction mixture 2, mix 0.5 ml apple juice extract (the enzyme) with 2.0 ml catechol in water.
3. **Run 3:** For reaction mixture 3, mix 0.5 ml apple juice extract (the enzyme) with 2.0 ml of catechol solution in buffer.

In your lab notebook before doing the experiment, sketch a graph showing the predicted absorbance vs. time trace for all three mixtures on the same axis.

Thinking About the Data from Part I

*Note, there is a CoLab tutorial available for data analysis, but you may use any software you prefer.

1. Make a table that summarizes the components of the reaction mixtures (this was part of the pre-lab assignment - update if necessary and add to your notebook).
2. Why is 0.5 ml of water added to reaction mixture 1?
3. Determine the initial rate of the reaction for each mixture, and record the results in your notebook in the same table as above.
4. Which reaction mixtures contain the catecholase enzyme? Based on your data, explain how the enzyme affects the rate of oxidation of catechol.
5. How does buffering the mixture affect the oxidation rate for the apple variety you selected?
6. Recall that apples contain catechol and catecholase. Based on your results, suggest one way to slow or inhibit the catalyzed browning of an apple.

Adapted from Cole, Renée S., Marc Muniz, Erica Harvey, Robert Sweeney, and Sally Hunnicutt. “How Should Apples Be Prepared for a Fruit Salad? A Guided Inquiry Physical Chemistry Experiment.” *Journal of Chemical Education* 97, no. 12 (December 8, 2020): 4475–81. https://doi.org/10.1021/acs.jchemed.0c00517.

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9.4: Part II, Does the type of apple matter?

In this part of this experiment you will compare the browning of several different types of apple. If more than one team is doing the experiment, decide which teams will work with which apples, and decide whether the experiment should be carried out in unbuffered solution, or using buffer to control pH. Provide justification for your answer.

One goal of physical chemistry is to develop mechanisms that explain the rate of a reaction. The Michaelis-Menten mechanism is often used to describe the kinetics of an enzyme-catalyzed reaction. The equation below derives from this mechanism:

$$v_0 = \frac{v_{\max}\ [S_0]}{K_M + [S_0]} \tag{9.4.1}$$

where v_0 is the initial rate, $v_{\max}$ and K_M are the maximum rate and the Michaelis-Menten constants, respectively, and $[S_0]$ is the substrate concentration.

Pre-lab assignment for Part II: Does the type of apple affect rate of browning?

📅 **Due before Wet Lab Meeting for Part II**

Complete any unfinished business from Part I, and review the reading and assignments from Part I.
Read pg 9.4 and complete the GENERAL PRE-LAB ASSIGNMENT for this part of the module. Then complete the following written assignment and submit your work before the deadline.

1. Identify the independent and dependent variables in Equation 9.4.1. What must be varied to determine $v_{\max}$ and K_M?
2. Examine Equation 9.4.1. Predict the appearance of a graph of initial rate, v_0 versus substrate concentration, $[S_0]$. Consider the dependence of the initial rate on low substrate concentration (as $[S_0]$ approaches 0) and high concentration (as $[S_0]$ approaches ∞).
3. Create a table similar to the one below in which you will add rows 2 through 7 (*this was part of the pre-lab assignment*). Keep in mind that the data analysis procedure amplifies the uncertainty in measurements made with low substrate concentrations. If you decide to run the reactions unbuffered, the last column gives the volume of water, and the substrate solution should be made in water. If you decide to run the reactions buffered, the last column gives the volume of buffer, and the substrate solution should be made in buffer.

Run #	**Volume of Enzyme**	**Volume of Substrate**	**Volume of Buffer or Water**
Run 4	0.50 mL	2.00 mL	0 mL
Run 5 ...	0.50 mL	...	...
Run 11	0.50 mL	0.125 mL	1.875 mL
Run 12	0.50 mL	0 mL	2.00 mL
Run 13	0 mL	2.00 mL	0.50 mL

4. How do Runs 12 and 13 differ from Runs 4 - 11? Why is it important to collect the data in Runs 12 and 13?

Part II Experiment : Does the type of apple matter?

Follow the protocol using the mixtures from the table. Then analyze your data and determine the v_{max} and K_M parameters for the enzyme extracted from your type of apple. There is a MatLab template provided to help you with this, but you may use any computational software you prefer.

Share your data with the rest of the class using the shared spreadsheet.

Discuss: Which type of apple is best for a fruit salad? What are the v_{max} and K_M parameters for the enzyme extracted from each type of apple, and how are these related to the selection of the type of apple that would be best for a fruit salad?

Thinking About the Data from Part II

*Note that there is a CoLab tutorial to help you through this, but you may use any software you prefer to accomplish this work.

1. Determine the initial rate of the reaction for each mixture and tabulate the results in your notebook.
2. If needed, calculate a "corrected" rate for trials 1-8 by subtracting the rates determined for the two controls (Runs 12 and 13). *This is usually not necessary.*
3. Create a graph showing the dependence of rate on substrate concentration. Ideally, all the rates should be plotted on the same axes. Describe in words how the substrate concentration affects rate, comparing your result to your predicted graph. Team members should reach consensus on a common description.
4. The kinetic parameters for this reaction may also be extracted directly from your graph of rate versus substrate concentration by fitting the data with a nonlinear equation of the form:

$$y = \frac{Cx}{D + x} \tag{9.4.2}$$

5. Explain the shape of this graph in terms of the Michaelis-Menton Equation.
6. We can simplify the determination of the kinetic parameters if we linearize the rate expression. Many scientists have found it useful to graph $\frac{1}{rate}$ or $\frac{1}{v_0}$ versus $\frac{1}{[S_0]}$ for mixtures with different substrate concentrations but constant enzyme concentration. Such a plot is often referred to as a Lineweaver-Burk plot. Show how the Michaelis-Menton equation can be linearized.
7. What are the slope and intercept of this linear graph?
8. Prepare a Lineweaver-Burk plot to extract the kinetic parameters of the catecholase/catechol reaction using the linearized equation.
9. Compare the Michaelis-Menton nonlinear fit to the Lineweaver-Burke linearization fit.
    a. Make a graph of [S] vs Initial Velocity with three data series: $v_0(expt)$ (symbols), $v_0(MMfit)$ (solid line), and $v_0(LBfit)$ (dashed line).
    b. To create the latter, you will need to transform the Lineweaver-Burke fit "back" to a Michaelis-Menton plot. Discuss with your classmates how you can do this.
    c. Create a residual plot for the experimental data compared to the two fits
    d. Discuss the conclusions you make from this graph in your notebook.
10. One person from your team should post the 'best' V_max and K_M values (derived from LB or MM) obtained and the type of apple analyzed in the shared data spreadsheet. Please be sure to enter the data carefully on the correct line of the spreadsheet. The other tema members should check the data entries to ensure they are accurate.
11. What are the units for your v_{max} and K_M values? Use the extinction coefficient of 1.03×10^4 L mol^{-1} for 1,2-benzoquinone at 540 nm to convert these to concentration units.

12. Compare the values of v_{max} and K_M determined using the Lineweaver-Burk plot and using non-linear curve fitting. Are there substrate concentrations for which one method provides a better fit?

13. Tabulate the v_{max} and K_M values for each type of apple (or other fruit) studied. Do these values predict that different types of apples (or other fruit) brown at different rates? Explain your answer. If possible, compare your tabulated results to those of others from your class, and use the class' values to support your answer.

14. What does the value of v_{max} tell you about the reaction? What does the value of K_M tell you about the reaction?

15. Suppose you want to make a fruit salad with apples. What factors would you consider when preparing the apples and the salad? Discuss based on your kinetics results.

Adapted from Cole, Renée S., Marc Muniz, Erica Harvey, Robert Sweeney, and Sally Hunnicutt. "How Should Apples Be Prepared for a Fruit Salad? A Guided Inquiry Physical Chemistry Experiment." *Journal of Chemical Education* 97, no. 12 (December 8, 2020): 4475–81. https://doi.org/10.1021/acs.jchemed.0c00517.

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9.5: Part III, Inhibition of catechol oxidation

Pre-Lab Assignment for Part III

Pre-lab assignment for Part III: What can inhibit the Browning of Fruit?

📅 **Due before Wet Lab Meeting for Part III**

Complete any unfinished business from Part II. REview the readings and your work from Parts I and II. Read pg 9.5 and complete the GENERAL PRE-LAB ASSIGNMENT for this part of the module. Then complete the following written assignment and submit your work before the deadline.

Files to support this experiment are here (click).

Please submit this assignment prior to the second scheduled lab period for this module. Submit it along with the general pre-lab assignment.

Although different varieties of apples (and other fruits) brown at different rates, they all turn brown eventually. To preserve fruit, a chef may choose a specific apple variety and add something (an inhibitor) or change a condition (temp or pH) to slow down or inhibit the rate of the browning reaction. Inhibitors are often listed as preservatives in recipes or on labels of fruits sold in cans or jars.

1. Suggest at least two possible inhibitors for this system or identify other conditions that could inhibit browning. Begin by looking for the preservatives used in recipes or on labels. Also, consider the results obtained in the first cycle of this experiment. Prepare to discuss your choice of inhibitors and/or conditions with your instructors.
2. Select a substrate concentration that falls in the (approximately) linear portion of the Michaelis-Menton plot, and write in your lab notebook the volume of substrate in the reaction mixture that resulted in this concentration.
3. The optimal concentration of inhibitor (or degree of inhibiting condition) must be determined experimentally; prepare to record the concentration of the stock inhibitor solution in your lab notebook. Create and complete a table similar to the one below (an example of an electronic version of a table is here (click)). The volume of substrate should be the same in each trial and should correspond to the volume you chose above (in pre-lab question 2). Try using concentrations of inhibitor in each mixture that vary by factors of 10. Get approval from your instructor before you actually use these for experiments. Depending on the selection of inhibitor, you may need to run the reactions without buffer.

Trial	Volume of Enzyme	Volume of Substrate	Volume of Inhibitor (Or degree of condition)	Volume of Buffer or Water
1	0.50 mL			
2	0.50 mL			
3	0.50 mL			

4. Each trial will be carried out in a cuvette. What is the best order in which to combine the enzyme, substrate, inhibitor, and buffer (if needed)? Explain your reasoning.

Experiment Part IIA: What can inhibit the browning of fruit?

In this phase of the experiment, you will answer the following two questions:

- What substance or condition do you choose to inhibit the rate of the browning reaction?
- What concentration of inhibitor or condition will slow but not completely shut down the reaction?

Follow the same general protocol as before to measure the rate of oxidation of catechol using the volumes of enzyme, substrate, inhibitor, and buffer or water determined in pre-lab question 3 above.

Thinking About the Data: Part IIA

1. Determine the initial rate of the reaction for each mixture and tabulate the results in a spreadsheet that may be shared with team members (or other class members).

2. Based on the results, decide which concentration of inhibitor slows the enzyme-catalyzed reaction without stopping the reaction completely.

3. Based on your results, how would you prepare apples for a fruit salad?

Experiment Part IIB: What type of inhibition is at play?

Inhibitors generally work according to one of the following mechanisms:

Equilibrium binding of an inhibitor, I, to the enzyme, E, to form an adduct, EI, as in the following equation:

$$\mathrm{EI} \rightleftharpoons \mathrm{E} + \mathrm{I} \quad K_1 = \frac{[\mathrm{E}][\mathrm{I}]}{[\mathrm{EI}]} \tag{9.5.1}$$

Equilibrium binding of an inhibitor, I, to the substrate-enzyme complex, ES, to form an adduct, ESI, as in the following equation:

$$\mathrm{ESI} \rightleftharpoons \mathrm{ES} + \mathrm{I} \quad K_2 = \frac{[\mathrm{ES}][\mathrm{I}]}{[\mathrm{ESI}]} \tag{9.5.2}$$

Competitive inhibition occurs when a substance similar in structure to the substrate competes with the substrate for the active site on the enzyme, thus blocking the enzyme from forming a complex with the substrate. *Uncompetitive inhibition* occurs when a substance binds to the enzyme only after it is bound to the substrate. Non-competitive inhibition occurs when a substance binds to the enzyme away from the active site, but the enzyme may still bind the substrate. However, the enzyme's changed structure means that the enzyme is no longer able to catalyze the browning reaction. In general, inhibitors are selected because they may structurally resemble the reaction substrate (in this case, either molecular oxygen or catechol).

4. Considering the equations 9.5.1 and 9.5.2 above, explain in words how a substance, acting as an inhibitor, can slow the rate of the browning reaction.

5. Which equilibrium above corresponds to

    a. competitive inhibition?

    b. uncompetitive inhibition?

    c. Justify your answer.

6. Explain why non-competitive inhibition involves both equilibrium expressions.

7. If a substance slows an enzyme reaction via competitive inhibition, the

V_{max} remains the same and K_m is larger; if the reaction slows via uncompetitive inhibition, both V_{max} and

K_m are smaller; and if the reaction slows via non-competitive inhibition, K_m remains the same but V_{max} is smaller. Examine your graph of initial rate versus substrate concentration. In your notebook draw three similar graphs (initial rate versus substrate concentration) showing the

effect of

a. competitive inhibition,

b. uncompetitive inhibition, and

c. non-competitive inhibition.

8. Complete three tables similar to the one below. It is only necessary to carry out six total trials (six different concentrations of substrate) rather than the eight used in Experiment Part I. In the first table the volume of inhibitor is that determined in #2 above (Thinking About the Data Part IIA). In the second table the volume of inhibitor is about half of that in the first table. In the third table the volume of inhibitor is about double that in the first table. Depending on your selected inhibitor, either water or buffer will be added to bring the reaction mixtures to a volume of 2.5 ml. Get approval from your instructor or teaching assistant before continuing.

Trial	Volume of Enzyme	Volume of Substrate	Volume of Inhibitor	Volume of Water or Buffer
1	0.50 mL			
...	0.50 mL			
6	0.50 mL			
7	0.50 mL	0 mL		
8	0 mL	2.00 mL		

This cycle requires the most data collection. It is hoped that students, having done the experiment four times, will be efficient.

Experiment IIB:

What is the most likely inhibition mechanism for your selected inhibitor? Carry out the same protocol as previously, but using the solution mixtures from the three tables in #8 above.

Thinking About the Data: Part IIB

9. Determine the initial rate of the reaction for each mixture and tabulate in a spreadsheet.

10. Construct graphs of initial rate versus substrate concentration for each concentration of inhibitor. Compare to your predicted curves for each type of inhibition.

11. Incorporation of the inhibitor processes into the Michaelis-Menten mechanism yields the following equation:

$$v_0 = \frac{v_{\max}\ [\mathrm{S}_0]}{\left(1 + \frac{[\mathrm{I}]}{K_1}\right) K_m + \left(1 + \frac{[\mathrm{I}]}{K_2}\right) [\mathrm{S}_0]} \tag{9.5.3}$$

where $[I]$ is the concentration of inhibitor. Invert this equation to find the inhibitor version of the Lineweaver-Burk equation.

12. Show that $1 + \frac{[I]}{K_1} > 1$ and $1 + \frac{[I]}{K_2} = 1$ for competitive inhibition. Go on to determine the slope and intercept of a Lineweaver-Burk plot for competitive inhibition.

13. Show that $1 + \frac{[I]}{K_1} = 1$ and $1 + \frac{[I]}{K_2} > 1$ for uncompetitive inhibition. Go on to determine the slope and intercept of a Lineweaver-Burk plot for competitive inhibition.

14. For non-competitive inhibition, $1 + \frac{[I]}{K_1} = 1$ and $1 + \frac{[I]}{K_2} = 1$. What are the slope and intercept of the resulting Lineweaver-Burk plot?

15. Construct and overlay the Lineweaver-Burk plots for the three inhibitor concentrations and tabulate the slopes and intercepts.

16. Decide the mechanism of inhibition for your inhibitor and explain your decision.

Adapted from Cole, Renée S., Marc Muniz, Erica Harvey, Robert Sweeney, and Sally Hunnicutt. “How Should Apples Be Prepared for a Fruit Salad? A Guided Inquiry Physical Chemistry Experiment.” *Journal of Chemical Education* 97, no. 12 (December 8, 2020): 4475–81. https://doi.org/10.1021/acs.jchemed.0c00517.

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9.6: Part IV, thermal stability of catalase (under construction)

Experiment Part III

In this part of the experiment, you will measure the effect of your inhibitor on the thermal stability of purified catalase. (under construction) The stability of proten folding can be modified by ligan binding, metal binding, pH, among other factors. One way to determine how an inhibitor may affect an enzyme is to monitor changes in the thermal stability of the protein upon ligan binding. In general, ligands that bind to a protein increase its stability.

Thinking About the Data: Part III

1. Quesitons under construction

Adapted from Cole, Renée S., Marc Muniz, Erica Harvey, Robert Sweeney, and Sally Hunnicutt. “How Should Apples Be Prepared for a Fruit Salad? A Guided Inquiry Physical Chemistry Experiment.” *Journal of Chemical Education* 97, no. 12 (December 8, 2020): 4475–81. https://doi.org/10.1021/acs.jchemed.0c00517.

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9.7: Experimental Procedure for Parts I - III

This is the protocol for using the Genesys 20 UV-vis to monitor the progress of an enzyme-catalyzed reaction.

Materials:

Caution

*Catechol is toxic and is an irritant. Wear PPE and avoid contact.

Chemicals and reagents: You will be provided with the following stock solutions:

1. Potassium phosphate buffer, 100 mM, pH 6.5 (~50 mL)
2. Solution of substrate (catechol) in water. (~50 mL)
3. Solution of substrate (catechol) in 100 mM phosphate buffer, pH 6.5 (~50 mL)
4. Apples of different varieties (or alternate fruit/vegetable)
5. Ice bucket with ice
6. Ultrapure water (~250 mL)

Instruments and equipment:

1. A Thermo Genesys 20 single-wavelength spectrometer.
2. A regular kitchen blender
3. A container to collect apple extract
4. Filter paper (coffee filter)
5. A funnel (to be used for gravity filtration)
6. Automatic Volumetric pipettes
7. Pipette tips of the appropriate size
8. At least two glass cuvettes (see sample cell below*)

***Sample Cell:** You will use a standard 1-cm cuvettes. We prefer that you use *glass* cuvettes when possible (glass is optically transparent to visible light, but not UV light).

Policy on use of Cuvettes

The glass and quartz cuvettes are *expensive and fragile*. You will treat them carefully and follow the policy below so that these precious tools do not become damaged.

- At all times, **cuvettes should be held in a rack at least 12 inches away from the edge of a bench**. Never place a cuvette directly on the bench.
- When pipetting, the cuvette is held at eye level so that the user can see that they are not damaging the cuvette with the pipette tip.

Preparation of Enzyme solution from Whole Apples

1. Prepare a solution of catecholase from apples (or alternate fruit/vegetable) in cold water.
   i. Peel and core one apple (or alternate fruit/vegetable). Discard the peel and the core.
   Peeling is optional, but it can reduce the background absorbance, so it is recommended. However you prepare your fruit, record it in your notebook.
   ii. Put the apple flesh into a blender with approximately 200 ml (total) of crushed ice and water.

iii. Puree the apple and ice until the fruit is pulverized.
iv. Pour the puree immediately into a beaker, rinse the blender so the next group can use it.
v. Extract the juice from the puree.
vi. Keep the extract on ice to slow the browning.

Keep the apple extract well mixed. Stir or gently shake it before each use so particles do not settle. If the solution is not mixed, early trials will contain more particles than later ones. Some of the PPO enzyme is attached to apple tissue, so these small particles are needed in the extract.

---

pH measurement

For selected experiments, use a pH strip or pH paper to measure the pH of the solution in the cuvette immediately after collection of kinetic data, and record the results in your data table. You may assume that experiments with similar solution components will have similar pH, and thus you only need one or two representative examples of pH for all your experiments.

Collection of Kinetic Data

The cuvette should be clean and dry before adding solution (or buffer or water for the blank). In the measurements that follow, the absorbance should never fall below zero or go above 3. If it does, record a new blank.

Prepare the spectrometer

Follow the instructions below to prepare the spectrometer for monitoring absorbance at 540 nm and to set up the software so that it is running in absorbance vs. time mode. Record the spectrum of the blank according to the instructions for your spectrophotometer. T

1. **Turn on the Genesys 20** and let warm up for ca. 15 minutes. Set the wavelength to the appropriate value using the buttons on the instrument (see instructions).



   - Start Spectra Pro on the computer by clicking the icon. The main screen appears.
   - Notice the buttons: 

   - Notice that the software recognizes the instrument and puts the name (20 Genesys) in the button bar. *Alert your instructors if this is not true in your case.*

2. Click on the **A vs Time** button. Read the Experiment Notes box and then click OK.
3. The **Setup** window appears:
   Set up the spectrometer to record absorbance every 2 seconds for about 180 seconds. Note that to collect every 2 seconds, the Sampling Rate should be 0.5 point per second.
   Click OK.

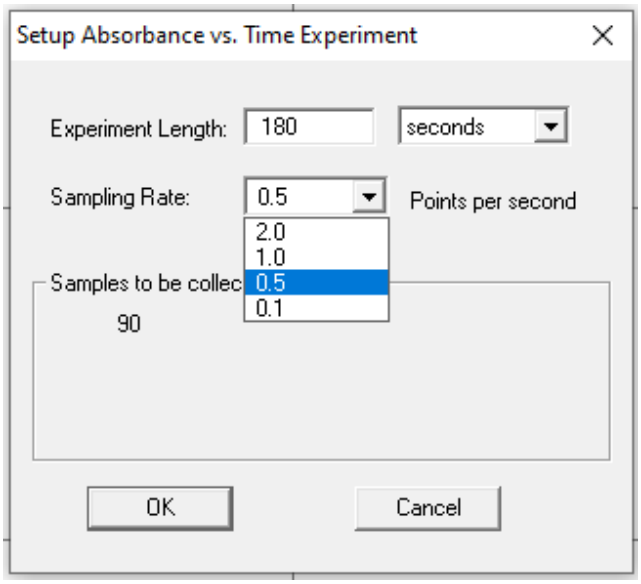


Figure 9.7.1: Setup window in SpectroPro software. (CC-NC-BY-SA; Kathryn Haas)

4. A **Calibration** window appears. Read the instructions.

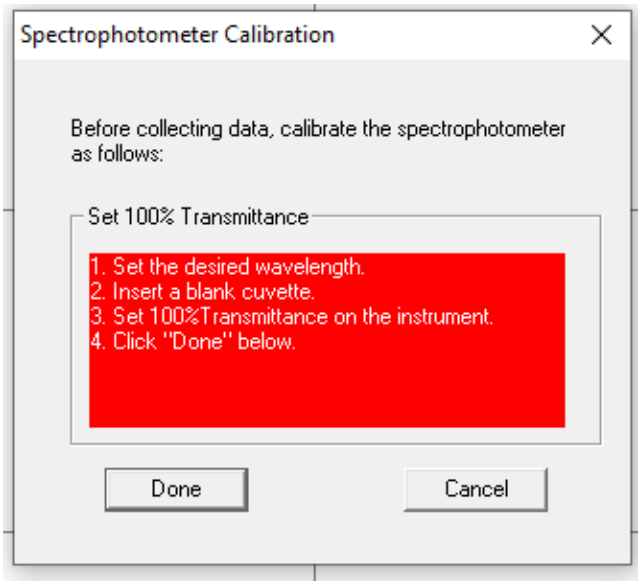


Figure 9.7.2: Calibration window. (CC-NC-BY-SA; Kathryn Haas)

i. Set the desired wavelength using the instrument control buttons (if you have not already done so).
ii. Insert a "blank" cuvette: Fill a clean *glass* cuvette with buffer. Wipe any fingerprints off the clear (i.e. not frosted) windows of the surface. Insert the cuvette into the Genesys with the light path going through the clear windows; close the cover.
iii. Press the 

button on the 20 Genesys to zero the instrument. Click Done in Spectra Pro. Remove the “blank” cuvette from the instrument and set it aside for later use. NOTE: *these cuvettes cost ca. $100 each; please handle them with care and respect.*
iv. Press Done.

Note: Sample Prep

The total volume of liquid in the cuvette must be 2.5 ml. Pipette the appropriate volume of stock catechol solution into the cuvette. Add the desired volume of buffer or water. Then later, quickly add 0.50 ml of enzyme solution (juice) to the same cuvette, and rapidly mix well using the tip of a Pasteur pipette.

Begin recording absorbance data *just before* mixing the final component of each solution.

5. **Ready the solution (but do not add enzyme yet)**:
   Add the appropriate amounts of Buffer and Substrate to another clean glass cuvette. Again insert the "blank" cuvette (containing only buffer) into the instrument to check the zero (absorbance should read 0.000). Re-zero the instrument if necessary.
6. **Ready the instrument:** Open the cover of the instrument. Click the 

button in the Spectra Pro software.
7. **Add enzyme** to substrate solution **and monitor reaction**:
   **Keep apple extract well mixed over the duration of these experiments (see above)*
   a. Draw up the enzyme solution. In a smooth, efficient but not rushed manner, add the enzyme to the cuvette. Draw the reaction mixture up into the pipet tip two or three times to thoroughly mix the contents.
   b. Wipe any fingerprints off the clear (i.e. not frosted) windows of the cuvette surface.
   c. Place the cuvette into the instrument with the light path going through the clear windows.
   d. Close the cover. (NOTE: Step 6 should be accomplished within ca. 15 – 20 seconds.)
8. **Collect and SAVE data:** Let the data collection run until finished. During the a run with enzyme, you should see a smooth increase in absorbance similar to that shown in the figure below. Notice that there is always a "Live" readout of the absorbance in the box at the lower right of the screen, and that the graph and data table is generated in real-time during the run. Notice also that in the run shown here, the first 20 seconds of the run has zero absorbance. This is the time it took to add the enzyme, mix the contents and insert the cuvette into the instrument.

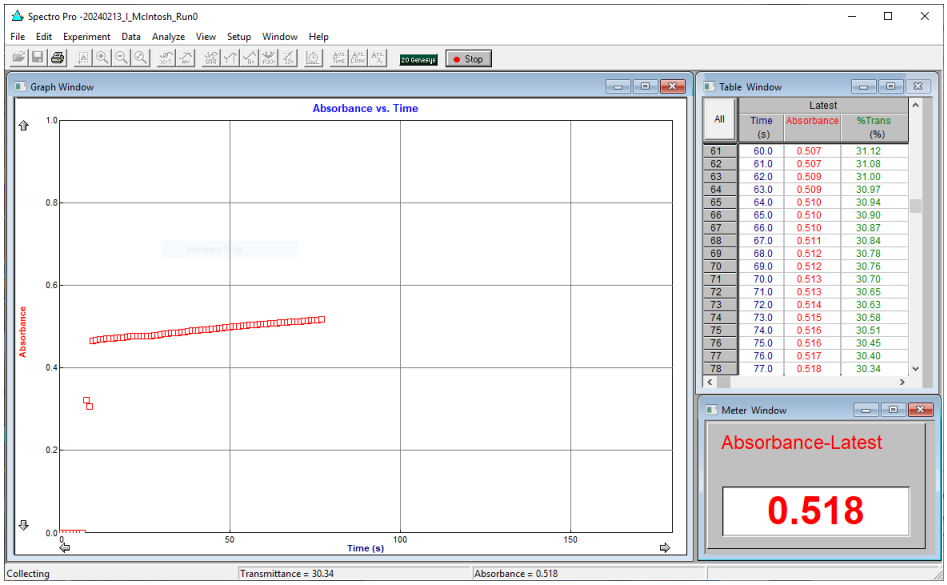


Figure 9.7.3: Copy and Paste Caption here. (CC-NC-BY-SA; Kathryn Haas)

9. Save the data in TWO FILE FORMATS (just in case!) within the data directory (c:\data\Chemistry 301L):
   a. Spectro Pro file using file name YYYYMMDD_Part#_APPLEVARIETY_Run#.sbl
   b. Text file using file name YYYYMMDD_Part#_APPLEVARIETY_Run#.txt

> **Note**
>
> **NOTE:** To save a text file, choose **Export Data** from the **File** menu and save a **.txt** copy of the data, using the same root filename (i.e., runLNX.txt). This file should also be saved in the data directory.

10. From the **Data** menu (top) choose **Store Latest Run**. Notice that this moves the latest data to the right in the Table Window.
11. Repeat the steps above as necessary for each sample.

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9.8: Post-Lab

Post-lab questions for ELN

Include your answers to the following post-lab questions in your electronic laboratory notebook (ELN).

1. Using a biochemistry or physical chemistry textbook, review the derivation of the rate equation for the Michaelis-Menten mechanism. What are the assumptions made?
2. Suppose someone prefers the taste of an apple that browns rapidly. What could be done to inhibit the catalyzed browning reaction for that apple? Suggest an experiment that could be done to determine the Michaelis-Menten kinetic parameters for this reaction.
3. How does pH affect the catalytic effectiveness of an enzyme? Suggest an experiment that could be done to determine the effect of acidity on an enzyme's ability to catalyze a reaction.
4. Use two of the references listed in the References section to discuss the role of the enzyme catecholase in the browning of fruit.

The materials in this module are adapted from Cole, Renée S., Marc Muniz, Erica Harvey, Robert Sweeney, and Sally Hunnicutt. "How Should Apples Be Prepared for a Fruit Salad? A Guided Inquiry Physical Chemistry Experiment." *Journal of Chemical Education* 97, no. 12 (December 8, 2020): 4475–81. https://doi.org/10.1021/acs.jchemed.0c00517.

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9.9: References

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10: CALORIMETRY

10.1: Pre-lab Assignment
10.2: Introduction to calorimetry
10.3: Solution Calorimetry
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10.4: Bomb Calorimetry
10.4.1: Introduction to bomb calorimetry
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10.4.5: Calculations and Discussion

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10.1: Pre-lab Assignment

Please complete the usual pre-lab assignment; there are no additional tasks for the calorimetry experiments. The description of usual pre-lab assignments is copied below for reference.

14.1.2.2: Assignment Details

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10.2: Introduction to calorimetry

Note

There are two "traditional" calorimetry experiments that the you can choose from in this module (pending the availability of instruments). Both experiments apply the same fundamental theories of thermochemistry. But they differ in the type of thermochemical experiment:

- Solution Calorimetry is a **constant-pressure experiment**
- Bomb Calorimetry is a **constant-volume experiment**

General Theory

Definitions:

Terms:

- A **system** is the specific place where a reaction or process is occurring (eg inside calorimeter).
- The **surroundings** are outside of the system (eg the lab bench, air around the calorimeter).
- A **closed system** is one where no *matter* is exchanged to or from the surroundings. In contrast, an open system is one where material can enter or exit the system (like a car or the human body).
- An **isolated system** is a closed system where no energy is exchanged to or from the surroundings.
- **Work (w)** is the energy associated with moving matter or energy in a non-random direction (eg expanding a gas). $w = \text{opposing force} \times \text{distance moved}$. When the force is pressure and the distance moved is related to volume, $w = -PdV$
- **Heat (q)** is the energy transferred as a result of temperature differences. Heat is associated with rotational and translational movement in random directions.
- Total energy (E) is the capacity to do work.
- **Internal energy (U)** is the internal energy of a system.

Symbols:

- $U =$ the internal energy of a system
- $q =$ heat
- $w =$ work
- $H =$ enthalpy
- $P =$ pressure
- $_p$ subscript means at constant pressure
- $V =$ volume
- $_v$ subscript means at constant volume
- Δ means the change in something (eg ΔY is change in Y)
- d means the differential (eg dH is the ordinary derivative of H)
- ∂ means the partial derivative

Energy

Energy is absorbed or released during chemical changes. Thermochemical studies involve the measurement of that energy as heat absorbed or evolved during a chemical change. This permits quantification of the energy released or absorbed in the making or breaking of chemical bonds.

The first law of thermodynamics states that energy is conserved. If energy enters a system, an equal amount must be lost by the system's environment. In the case of a closed system, the energy change for a system may be written as follows:

$$\Delta U = q + w \tag{10.2.1}$$

where ΔU is the internal energy change of the system, q is the heat entering or leaving the system, and w is the energy change caused by work.

If work is done on the system by an external source, this would result in an increase in the internal energy of the final state, thus w in Equation 10.2.1 would be a positive quantity; if the system were to do work on its surroundings, w, would be negative. If q is positive, heat has entered the reaction system and the reaction is *endothermic*. Conversely, if q is negative, the reaction is *exothermic*.

In chemical reactions, work is most often from changes in volume (V) due to a change in the moles of gas. Expansion work is expressed as $w = -PdV$, where pressure (P) and volume (V). Thus, 10.2.1 can be written:

$$\Delta U = q - PdV \tag{10.2.2}$$

Constant volume

In a constant volume experiment, no work is done, this $\Delta U = q$.

Let's take the combustion of glucose as an example. If glucose is combusted to form six molecules of carbon dioxide gas, the volume expands. Some of the energy released from the chemical reaction is heat, while some does expansion work. However, when a system has rigid walls (like a bomb calorimeter), and thus the volume does not change, no expansion work is done; thus all energy is transferred as heat, and $\Delta U = q$.

In this case, **we can measure the energy gained or released by a chemical reaction by measuring heat**; or temperature change. The heat is related to the measured temperature change (ΔT) by the calorimeter by the calorimeter's heat capacity (C_{cal}):

$$C_{cal} = \frac{q}{\Delta T} \tag{10.2.3}$$

Where $\Delta T = T_{\text{final}} - T_{\text{initial}}$

At constant volume, we can also express this as $C_{v,cal} = \dfrac{\Delta U}{\Delta T}$, where the "v" subsript indicates constant voume.

Provided that the C_{cal} is known, the heat q, and thus energy of the reaction ΔU, can be determined by measuring ΔT before and after the chemical reaction has occurred.

Enthalpy

The enthalpy (H) of a system is defined as $H = U + PV$, where U is the internal energy of the system, P is pressure, and V is volume. We can also define a change in enthalpy as a change in each of the component state functions:

$$\Delta H = \Delta U + P\Delta V \tag{10.2.4}$$

Enthalpy at constant pressure

Enthalpy lets us keep track of the energy of a system that is at constant pressure (like our solution calorimeters). And using 10.2.1 we can write this expression as a function of heat and work:

$$\Delta H = q + w + P\Delta V \tag{10.2.5}$$

And we can substitute the expression $w = -P\Delta V$ into this expression to show that $\Delta H = q$:

$$\Delta H = q - P\Delta V + P\Delta V = q \tag{10.2.6}$$

Just as the case described above, we can determine q from a measurement of ΔT using a known heat capacity for the calorimeter. At constant pressure, the calorimeter's heat capacity can be expressed as $C_{p,cal} = \dfrac{\Delta H}{\Delta T}$, where the "p" subscript indicates constant pressure. Thus, it is clear that the change in enthalpy can be determined by measuring ΔT. However, this is not a direct measure

of ΔU, because at constant pressure, some work may be done if there is a change in volume.

Enthalpy involving gas

When a gas is evolved as a product of the chemical reaction, the volume change, and the work done is significant. A relationship between ΔH and ΔU can be determined with some help from the ideal gas laws:

$$\Delta H = \Delta U + \Delta n_{gas} RT \tag{10.2.7}$$

where Δn_{gas} is the change in the moles of gas from reactants to products.

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10.3: SOLUTION CALORIMETRY

10.3.1: Introduction
10.3.2: Instrumentation
10.3.3: Experimental
10.3.4: Data Analysis
10.3.5: Discussion questions

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10.3.1: Introduction

In this experiment, you will determine the standard enthalpy changes for a series of reactions of the following type:

$$\mathrm{MX}_{(s)} - \longrightarrow \mathrm{M}_{(aq)}{}^{+} + \mathrm{X}_{(aq)}{}^{-} \tag{10.3.1.1}$$

where $\mathrm{M}_{(aq)}{}^{+}$ is one mole of a cation, M^{+}, in an infinitely dilute aqueous solution and $\mathrm{MX}_{(s)}$ is one mole of the solid. The energy released when an ionic solid dissolves in solution is normally described as **heat of solution**.

When a solute is dissolved in a solvent, heat may be absorbed or evolved. The integral heat of solution is the enthalpy change for the solution of 1 mole of solute in n moles of solvent. When reporting heats of solution, the concentration of the final solution must also be stated. The integral heats of solution for $\mathrm{H_2SO_4}$, NaOH, and $\mathrm{NH_4NO_3}$ are plotted versus the amount of water per mole of solute in Figure $10.3.1.1$. As the amount of water is increased, the integral heats of solution reach limiting values and no further heat change occurs on addition of more water. Experimentally, the integral heat of solution at infinite dilution is found by measuring the integral heats of solution at progressively higher dilutions until the enthalpy change per mole of solute no longer changes. The integral heat of dilution is the heat liberated or absorbed when a solution of known concentration is mixed with a sufficient amount of solvent to produce a more dilute solution of new and known concentration.

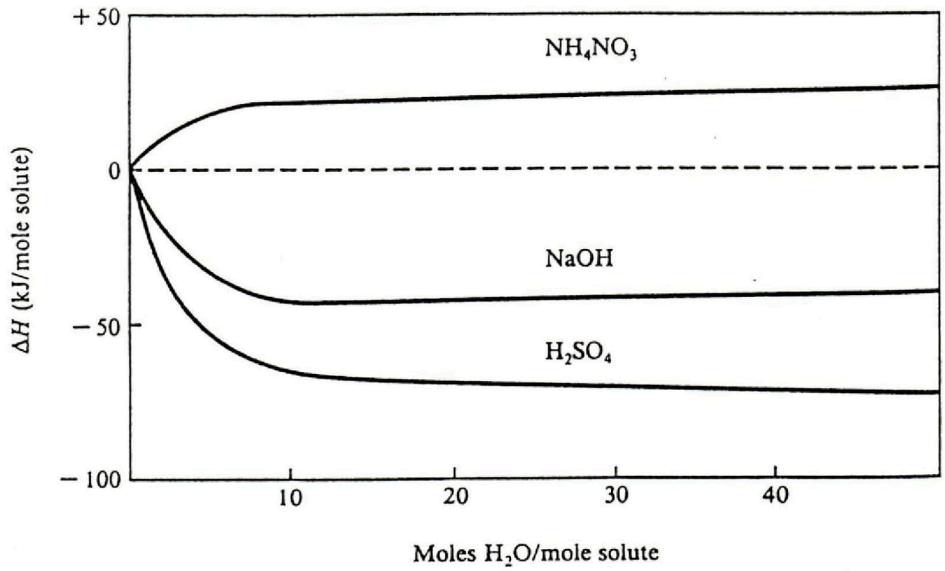


Figure $10.3.1.1$: **Integral heats of solution.**. (Duke Chem)

Heat capacities relate the differential transfer of heat in a system to its differential temperature change, $dq = CdT$, and are usually expressed on a molar basis. If a process is carried out at constant pressure, the heat capacity is designated as C_p, and, since the heat capacity itself may be a function of temperature, the heat involved would be given by:

$$q_p = \int_{T_1}^{T_2} C_p dT \tag{10.3.1.2}$$

The reaction in this experiment is performed under constant (atmospheric) pressure in a thermally insulated calorimeter. Thus, the reaction conditions are adiabatic (q_p = 0) and not isothermal (constant temperature). The relationship between isothermal and adiabatic conditions is shown in Figure $10.3.1.1$. Enthalpy is a state function and therefore ΔH is independent of the path taken (in general q is not). Therefore

$$\Delta H = \Delta H\left(T_1\right) + \int_{T_1}^{T_2} C_p dT \tag{10.3.1.3}$$

where $\Delta H\left(T_1\right)$ is the enthalpy change for the isothermal part of the path shown in Figure $10.3.1.2$. The temperature change for the reaction is generally small enough for C_p to be considered constant and therefore Equation $10.3.1.3$ becomes $10.3.1.4$:

$$\Delta H = \Delta H\left(\Delta H\right) + C_p\left(T_2 - T_1\right) \tag{10.3.1.4}$$

Under adiabatic conditions, $\Delta H = qp = 0$ and thus Equation 10.3.1.4 simplifies to 10.3.1.5:

$$\Delta H_{T_1} = -C_p\left(T_2 - T_1\right) \tag{10.3.1.5}$$

and finally

$$\Delta H\left(T_1\right) = -\left[C_{p,cal} + C_{p,\text{ products}}\right]\left(T_2 - T_1\right) \tag{10.3.1.6}$$

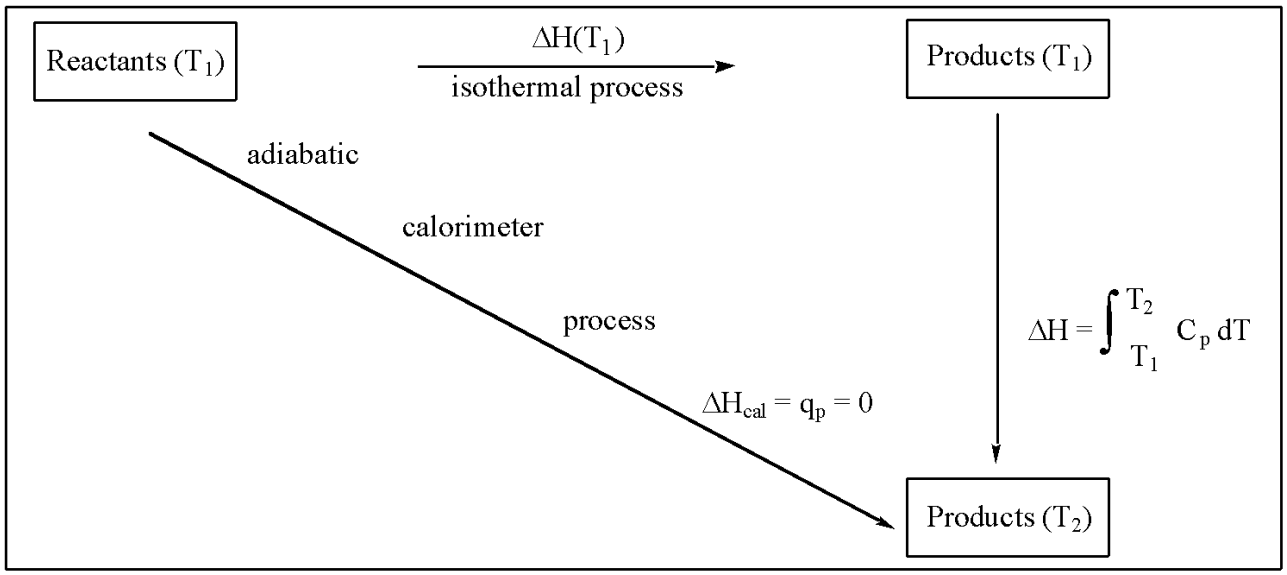


Figure 10.3.1.1: Thermochemical changes in calorimetric system at constant pressure. ΔH = enthalpy change for calorimeter process; T_1 = initial temperature; T_2 = final temperature; $\Delta H\left(T_1\right)$ = enthalpy change for imagined isothermal process (reactants and products at T1); (C_p) = heat capacity (at constant pressure) of the contents (($C_{p,products}$)) and inner walls of the calorimeter, (($C_{p,cal}$)) after the reaction has occurred. (Duke Chem)

The enthalpy change, which occurs upon dissolution of TRIS (tris(hydroxymethyl)amino-methane hydrochloride) in aqueous hydrochloric acid, or of KCl dissolved in deionized water, is known with precision. The heat capacity of the products is given by the product mass multiplied by its specific heat capacity, which for aqueous solutions is assumed to be $4.18\ J\ K^{-1}\ g^{-1}$. Therefore, if one measures the temperature change (T_2 - T_1) that occurs during either of these reactions, the heat capacity of the calorimeter at constant pressure ($C_{p,cal}$) may be determined. Knowing ($C_{p,cal}$), we can measure the heat of solution (enthalpy change ΔH_{T_1}) of other salts by measurement of the temperature change during the reaction.

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10.3.2: Instrumentation

APPARATUS: Parr 6755 Solution Calorimeter; Parr 6772 Calorimetric Thermometer; PC computer; lead donut; 100 mL pipet; pipet bulb; Analytical Balance (check uncertainty); and, flask of room temperature DI water.

REAGENTS: KCl(solid); CH3COONa (solid); CH3COONa.3H2O (solid); NaCl (solid).

NOTE: All solid samples (with the exception of CH3COONa.3H2O) should be ground to a fine powder, oven dried and cooled in a desiccator prior to use.

The Parr 6755 Solution Calorimeter

The solution calorimeter consists of a rotating sample cell and an insulated Dewar flask (see Figure 3). The rotating cell holds 20 mL of liquid sample or up to one gram of solid powder sample. Chemical reaction is initiated by pressing the glass push-rod against the bottom of the rotating cell and dropping the reactant in the rotating cell into the Dewar. The rotating cell is stirred vigorously and the reaction proceeds to completion. **The rotating cell and push-rod assembly is extremely fragile and should be handled and used with care at all times.**

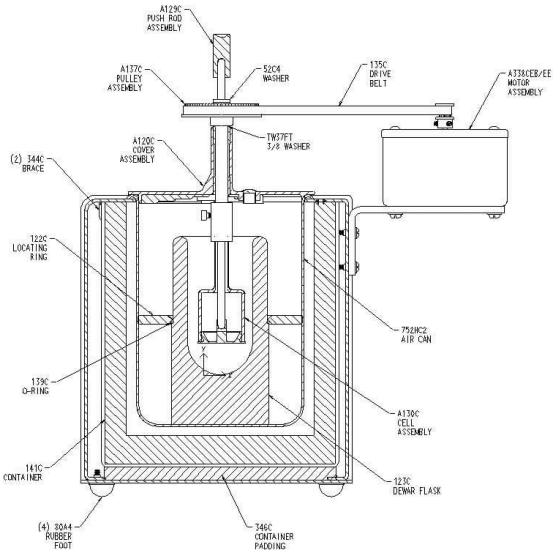


Figure 10.3.2.1: Diagram of The Parr 6755 Solution Calorimeter (Copyright; author via source)

PRECISION: The precision obtainable with the 6755 Solution Calorimeter will be a function of the amount of heat liberated by the reactants and the temperature at which the test is conducted. The best precision will be obtained when working with reactions that release between 200 and 600 calories, producing a temperature rise of 1.5° to 5°C at or near room temperature. Under these conditions a standard deviation of less than 0.4% of the determined value can be obtained in repetitive tests. If the total heat release produces a rise of less than 0.5° or more than 6°C, or if the test is conducted at higher working temperatures with significant heat leak, the relative standard deviation may increase to 1.0% of the determined value.

Specifications For The 6755 Solution Calorimeter	
Working temperature range	10° to 50°C
Temperature sensitivity	0.0002°C

Specifications For The 6755 Solution Calorimeter	
Energy measurement range	2 to 1000 calories
Detectability limit	0.1 calorie
Energy equivalent	100-145 calories/°C
Maximum volume, solute	20 mL
Required volume, solvent	90 to 120 mL

Specifications For The 6772 Calorimetric Thermometer	
Range:	0-70°C
Resolution:	0.0001°C
Absolute accuracy: Without calibration With calibration	+/- 0.100°C +/- 0.050°C
Repeatability: Single point	+/- 0.002°C
Linearity: 10°C span	+/- 0.002°C

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10.3.3: Experimental

In lab, you will calibrate the calorimeter using two trials and potassium chloride (KCl) as the calibration standard. Then you will measure the heat released upon dissolution of three salts: anhydrous sodium acetate, hydrated sodium acetate, and sodium chloride (NaCl).

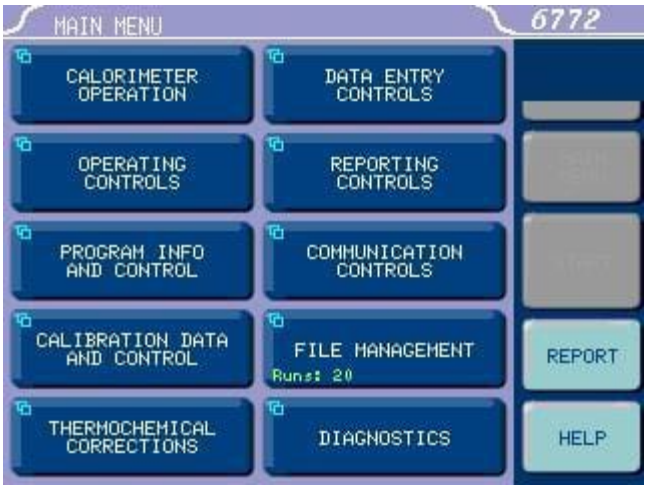
Preparing the instrument and sample

1. **Load solvent in the calorimeter:**
   Prepare a large flask with ultrapure water and allow it to come to room temperature. The calorimeter's Dewar flask has a capacity of approximately 100 mL and must be filled with not less than 90 mL but not more than 120 mL of solvent. Use a volumetric 100.00 mL pipet to transfer 100.00 mL of ultrapure room temperature water into the Dewar flask.
   *Volumetric pipets are "Class A" glassware, and the errors associated with their measurements can be found either on the flask itself or in a table of tolerances (like this one, click).
2. **Loading samples into the rotating cell:**
   It is extremely important that you fill the cell carefully and that no sample is lost or place in the incorrect place in the sample dish. If you do spill some of the sample, or if the cell leaks, clean out the cell and start again.
   a. **Loading by weight (solid or liquid samples):**
      i. Disassemble the cell and tare the clean and dry bottom of the cell (a Teflon dish) on an analytical balance.
      ii. Take the Teflon dish out of the balance and add the solid sample directly to it.
      iii. Weigh the dish plus sample to obtain the sample mass.
   b. **Loading by volume (liquid samples):** Liquid samples can be loaded into the rotating cell either by volume or by weight.
      i. Disassemble the cell and tare the clean and dry bottom of the cell (a Teflon dish) on an analytical balance.
      ii. Set the Teflon dish on a flat surface and press the glass bell over the dish, handling the glass carefully as described above.
      iii. Fill the pipet with the solution to be added.
      iv. Carefully insert the pipet through the glass stem and add the solution to the rotating cell.
   c. **Assembling the sample cell, cover, pulley assembly and push rod:**
      1. Carefully assemble the **sample cell** by pressing the glass bell over the dish. To do this, place the dish on a flat surface and gently press the glass bell over the dish to assemble the cell. Do not hold the thin-walled glass stem during this operation–it is fragile and will break easily.
      2. Insert the stirring shaft (metal rod) through the cover assembly, and attach it to the cell assembly by sliding the white plastic coupling of the sample cell onto the metal shaft as far as possible. Tighten the thumb screw until it is finger tight.
      3. Insert the glass push rod very carefully and avoid disturbing the sample. With the dish again on a flat surface, insert the push rod through the pulley hub and gently press the end of the rod into the socket in the sample dish.
      4. When the entire assembly is prepared with sample, the thermistor probe can be placed in the hole in the sample cover and the entire assembly can be placed onto the calorimeter so that sample cell is lowerd into the Dewar flask with the cover in place on the air can.

Experimental Procedure

Set up the calorimeter

1. Switch on the Calorimetric Temperature Unit using the **on/off** switch at the rear left of the instrument.
2. After a short "Self Test" routine the following screen will appear.



3. Press **Operating Controls**. Look over the buttons. **Method of Operation** should be *Solution* and **Language** should likely be *English*.

Standardize the calorimeter with KCl (to determine C_p)

The purpose of this standardization is to **determine the heat capacity of the calorimeter (C_p)** by measuring the heat change in a well-characterized reaction. You will use the dissolution of KCl as the calibration standard. In the recommended standardization procedure, when **0.5000 –0.7000 grams of KCl** is dissolved in 100.00 mL of DI water, the reaction absorbs **230.98 joules per gram of KCl at 25 ˚C**.

Note

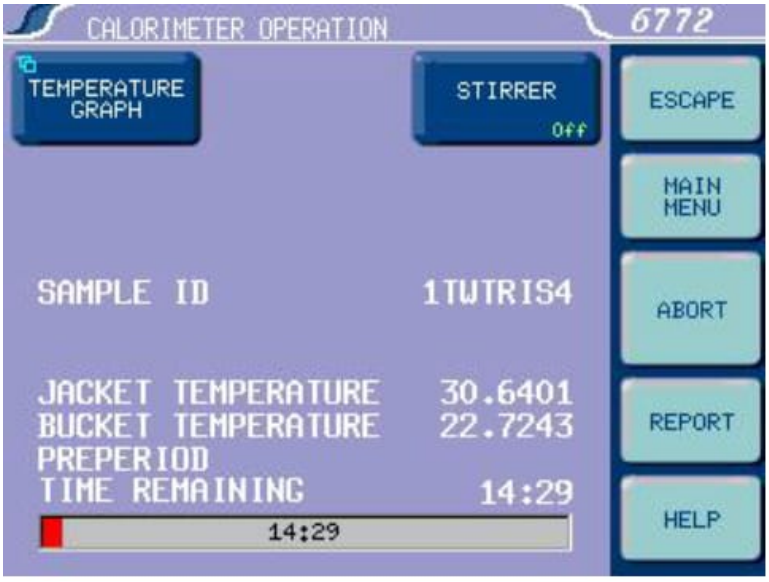
The KCl used in the calibratio should be oven-dried overnight at 80˚ C and cooled in a desiccator prior to use. Exposure of the KCl to air and moisture should be avoided in order to preserve the integrity of the standard.

Please return the KCl stock container to the desiccator immediately after use.

1. If you have not done so already, add exactly 100.00 ± 0.08 mL of ultrapure water to the Dewar flask.
2. Prepare the sample cell cover, pulley assembly and push rod as described above.
   i. Make sure that both components of the rotating cell (Teflon dish and glass bell) are clean and dry before use.
   ii. Be sure the bell jar is sealed against the teflon dish.
   iii. Weigh 0.5000 –0.7000 gram of your standard KCl into the clean, dry Teflon dish on an analytical balance to an accuracy of ± 0.0001g(or ± 0.0002 g, depending on the balanced used).
   iv.
3. Place the thermometer into the hole in the cover assembly, making sure not to distrub the cell.
4. Place the sealed sample cell into the Dewar (with water) so that the cover is in place over the calorimeter air can and the thermistor probe cord is moved out of the way of the pulley assembly.
5. Place the lead donut on the cover.
6. Place the drive belt over the pulleys.
7. On the calorimeter, press **Escape** or **Main Menu** to go back one screen to the main menu.
8. Press **Diagnostics**. The Data Logger should be off. If it is on, press the **Data Logger button to turn it off**. Press the **Delete Data Log File** button to clear the data log. Check to be sure that the Data Log Format is set to **Data Format (csv)**.



9. Press the **Start** button on the right side of the screen. The stirrer to the calorimeter should turn on automatically. You will be prompted to enter a Sample ID. If you like, use the format: initialsMMDD-N, where: initials are your initials; MMDDis the date; and, N is the number of the run (e.g., 1 for the first run). Press Enter when you are done.
10. Press the **Data Logger** button to turn data logging **on**. At this point your run has started and you are logging temperature and time data.
11. Press the **Main Menu** button on the right side of the screen. Then press **Calorimeter Operation**. You will be taken to a screen that shows the progress of the current run. You will see your sample run information along with the temperature inside the system (listed as the Bucket Temperature). At the bottom of the screen you will see a timer that will monitor the progress of the run.



12. Press the **Temperature Graph** button and a real-time image of the temperature inside the calorimeter (the Bucket Temperature) will appear.
13. Press **Setup** and you will see the following screen. Set the Bucket Min value ~0.4 degrees *below* the pre-period baseline temperature and Bucket Max value ~0.4 degrees *above* the pre-period baseline temperature. Press Escape when you are done.



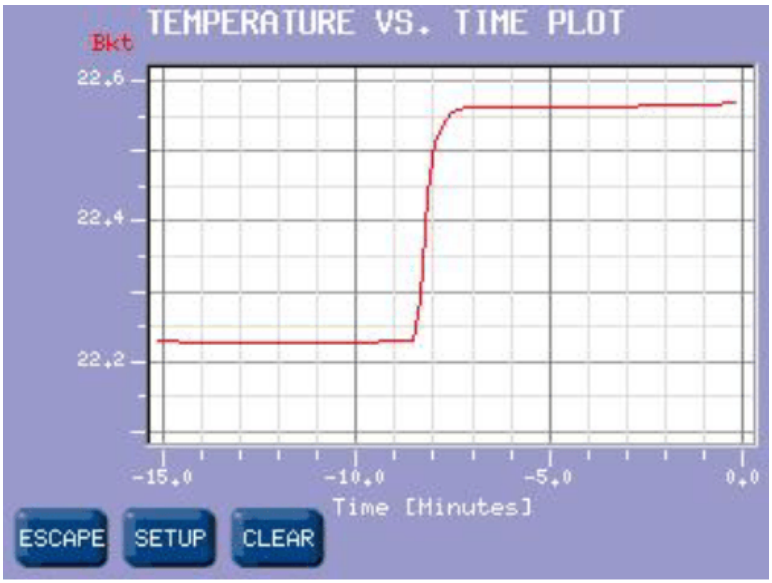
14. Go to the computer associated with the calorimeter. On the desktop, find the Parr Calorimeter shortcut. This will take you to a Web page associated with the calorimeter. Once there, click on the LCD Image tab and a screen shot of what is currently on the calorimeter display will appear. This is not a “living” image, but one that is captured at the moment you clicked the LCD Image button. To update the image, press the F5 key on the computer keyboard.



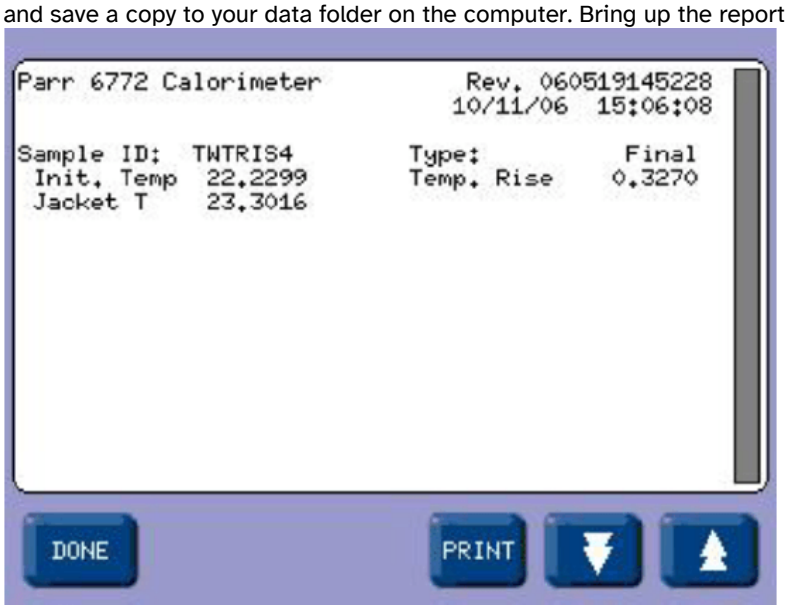
15. About seven minutes after starting the run you will hear a loud beep and the calorimeter will prompt you to “inject” the solid sample into the stirring solution. Do this by gently, but firmly, pushing down on the glass rod (NOTE: these are easily broken so please be careful). Then, press continue on the calorimeter.

> **"Timed out" error**
>
> If the calorimeter gives a "Timed out" error message, it likely means that the temperature was not stable during the first seven minutes. If this happens, check the bell jar to be sure it is assembeld correctly. If so, start the run again. If not, begin again by preparing a new sample.

16. Observe the temperature change inside the system by monitoring the **Temperature Graph** either on the calorimeter display or by updating the LCD Image on the computer screen. You want to watch the display for the first minute or two to be sure that the sample was, in fact, introduced properly into the solvent. If there was a problem with the mixing of solute and solvent (something that happens occasionally) you will get an error message on the calorimeter screen and the run will stop. If that happens clean out the system and try the run again.



17. Near the end of the run you will hear another beep from the calorimeter telling you the run has completed. Press F5 on the screen and capture the Temperature Graph on the computer screen at that moment. Right-click on the thermogram image and save a copy to your data folder on the computer. Bring up the report for the run save a copy of it as an image file.



18. Click on the **Home** button at the bottom of the browser window. Then Click on the Data Log tab. You will get a new window containing the logged data from the run. Each row contains the date, the time, the bucket temperature, the jacket temperature and two columns that are mostly zeros. Use Control-A to select the entire window; and, Control-C to copy it.
19. Open the Windows Notepad (Start ®Accessories ®Notepad) and Paste the data log into the Notepad window. Delete any text that may appear below the last row of data. Select **Save As** from the File menu and save the Notepad as a .txt file into your data folder.
20. Press Escape on the calorimeter screen and the report will disappear leaving the thermogram. Press Escape again and you will return to the Calorimeter Operation Screen. Press Main Menu on the button bar and then press the Diagnostics button to navigate back to the Diagnostics Screen. Press the Data Loggerbutton and when you get to the Data Logger screen andturn the Data Logger off.
21. Ask your TA to supervise as you carefully dismantle the calorimeter. First remove thermistor probe and wipe it dry. Then remove the glass push rod, wipe it dry and place it somewhere where it will not get broken. Carefully lift the cell assembly part way out of the Dewar flask and carry both the Dewar flask and the cell assembly over to the sink. Rinse the cell assembly briefly and then remove the cell from the shaft. Rinse the Dewar and the Teflon dish. Be extremely careful not to break the glass pieces –the glass cell costs ca. $135 and the glass push rods cost ca. $60 each.
22. Carefully dry the cell, inside and out and even up into the shaft. Dry also the Teflon dish, the Dewar, and the pieces of the top (metal shaft and top). Also, check the calorimeter and clean up any spills inside the aircan or on the surface of the calorimeter

itself.
23. Repeat the procedure with another sample of the calibration standard, and then once with each of the other samples.

File Names

Use the following convention when naming all files: initialsMMDD-N, where N is the number of the run (e.g., 1 for the first run).When naming files number each run according to the following table:

File name initialsMMDD-N	Description
initialsMMDD-**1**	First calibration with KCl
initialsMMDD-**2**	Second calibration with KCl
initialsMMDD-**3**	Sodium acetate
initialsMMDD-**4**	Sodium acetate trihydrate
initialsMMDD-**5**	Sodium chloride

Repeat the procedure for all samples

The general steps are listed below:

1. Pipet 100.0 mL of water into the Dewar flask.
2. Weigh accurately 0.7 -0.8 grams (weigh to nearest 0.0002 g) of solid sample into the Teflon dish.
3. Assemble the apparatus as before.
4. Conduct the runs exactly as you did during the standardization.
5. Repeat this procedure for remaining salts.

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10.3.4: Data Analysis

Calculation of ΔT_c from the thermogram using Logger Pro

You will use **Logger Pro** software to analyze at least one thermogram collected during the experiment. Logger pro is available on computers in the P-chem lab, and is also available from Duke OIT. However, versions later than 3.8.6 have trouble importing the .txt data files from the calorimeter. If you would like version 3.8.6 for your own computer, it is available on the course Sakai site.

The graph of temperature (T) versus time (t) produced in this experiment is called a thermogram and should resemble that shown in Figure $10.3.4.1$. Because the initial (pre-period) and final (post period) slopes of the thermogram may be different, and because the temperature rise due to a chemical reaction is usually nonlinear, it is necessary to decide on a procedure to best estimate the true net temperature rise in the experiment. A common method is to extrapolate the post period slope backward in time and the pre-period slope forward in time (the dotted lines in Figure $10.3.4.1$).

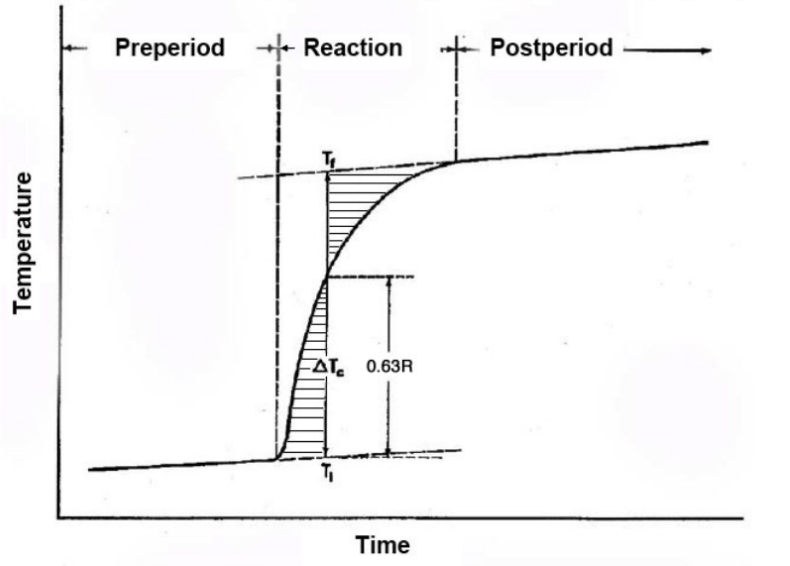
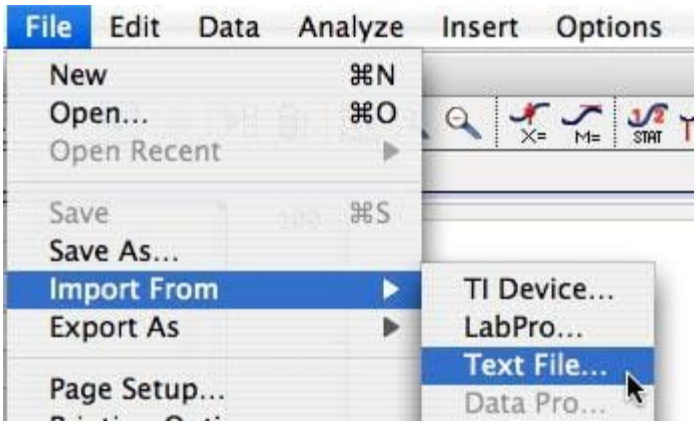


Figure $10.3.4.1$: ypical Temperature Rise Curve for 6755 Calorimeter. (Duke Chem)

The net temperature rise (ΔT_c) can be measured from the difference of these two extrapolated lines at some intermediate time in the reaction period. The exact location of this intermediate time depends on the calorimeter, and on the reaction being studied. A frequently used criterion for estimating this time is to measure ΔT_c at the point where the shaded areas in Figure 4 are equal. The temperature rise from the reaction increases exponentially with time, as $T = T_i + A(1 - e^{-kt})$, where A is the temperature rise (ΔT_c) and k is a constant. It can be shown that these two shaded areas will be equal when $t = \frac{1}{k}$, or when the temperature increase is approximately $0.63\Delta T_c$. This procedure usually works well for chemical reactions of the type studied here. A procedure for graphical analysis for determination of ΔT_c based upon this criterion is outlined below.

1. Start Logger Pro by Clicking on the  icon on the computer main screen. When the program loads, you will see a *Data Set* window on the left side of the screen and a *Graph* window on the right. Click once in the Graph window and then select **Graph Options** from the **Options** menu. Be sure that *Connect Points* is **not** checked. The *Point Protectors* option should be checked.

2. Select **Import From – Text File** from the **File** menu. When prompted, select your Windows Notepad (.txt) file for your first KCl run. The data will import directly into the *Data Set* window and the thermogram will appear in the *Graph* window.



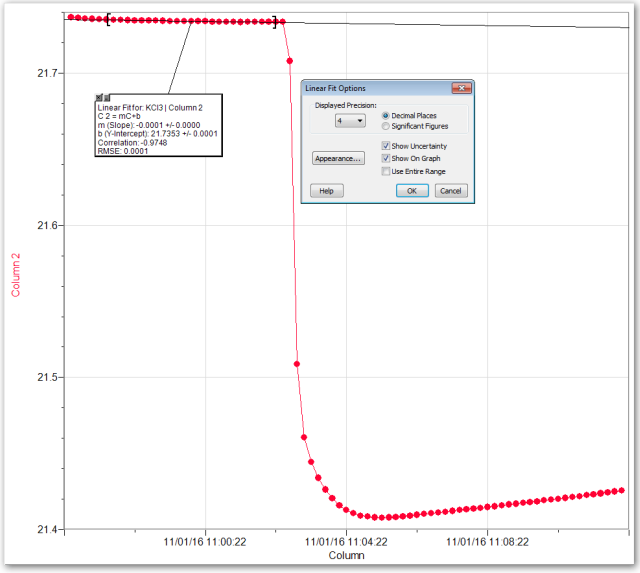
3. Look first at the *Data Set* window. Double Click on the **Column** heading above the first column of numbers. A dialog box will appear and you can change the name of the column from Column to **Time**. In the Units box enter **Seconds**. Repeat this procedure for Column 2 – changing it to **Temperature**. There is a Symbols entry box below the Units section where you will find the degree symbol so that you can enter **oC** for the units of the Temperature axis.



	Time (Seconds)	Temperature (°C)
1	/06 15:39:15	22.5418
2	/06 15:39:20	22.5418

4. Look now at the pre-period baseline. From within the Graph window, use the mouse to click and drag along a section of the pre-period baseline that accurately reflects the slope of this portion of the thermogram. The software will highlight the selected portion of the baseline. Click on the 

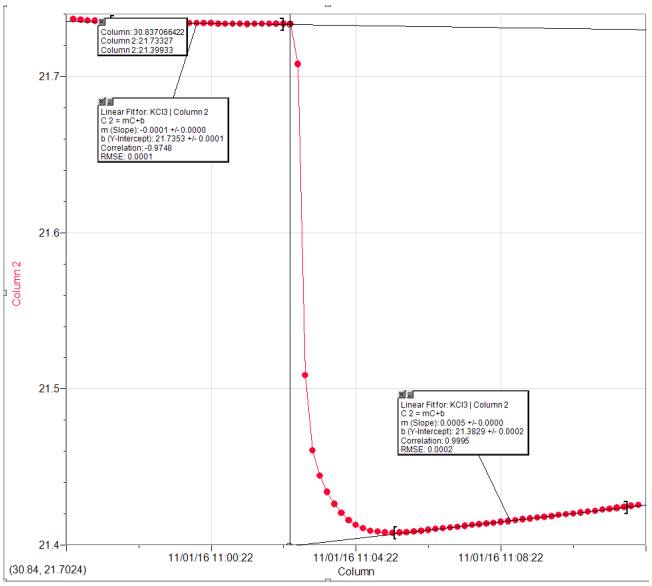
button in the button bar at the top of the screen. A Linear Least-Squares line will be calculated for the selected data. The results will be shown in a text box inside the graph window. You can move the text box to any position in the graph window with your mouse. Double-click inside this text box and an **Options** box will appear. Put checks in the **Slope** and **Intercept Standard Deviations** boxes and click **OK**. Now when you look at the Least-Squares results you will also see the associated uncertainties in slope and intercept.



5. Repeat step 4 procedure for the *post-period* baseline.

6. The Interpolate function in Logger Pro will be useful to find R and ΔT_c. To begin, Select **Interpolate** from the **Analyze** menu. A vertical bar running between the pre- and post-period Linear Least-Squares lines will now move with your cursor. In

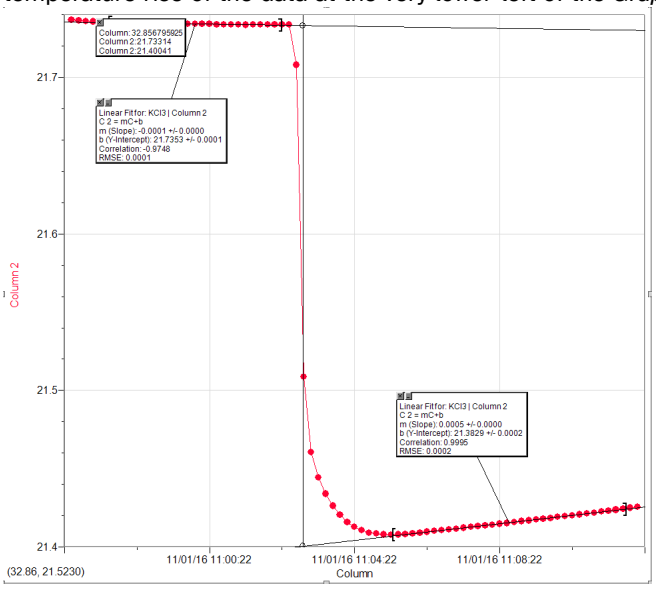
addition, a new text box appears which will show you the temperature of the pre- and post-period lines at the position of the bar.



7. Move the interpolation bar to a point close to the beginning of the reaction period (see the picture above and also Figure 10.3.4.1). Calculate R at this point by subtracting the final interpolated temperature from the initial interpolated temperature. In the picture above $R = 21.39938–22.73327 = –0.33385°C$. Multiply R by 0.63 and add this result to the initial interpolated temperature. In the example above:

$$T_{0.63R} = 21.73327 + (0.63(-0.33385)) = 21.52295°C \tag{10.3.4.1}$$

8. Move the Interpolation bar to the point where this temperature, T0.63R, intersects with the thermogram. You can follow the temperature rise of the data at the very lower-left of the *Graph* window.



9. Read the initial temperature (T_i) and the final temperature (T_f) at the points of intersection of this line with the pre- and post-period lines and subtract these to determine the corrected temperature rise (ΔT_c:

$$\Delta T_c = T_f–T_i \tag{10.3.4.2}$$

10. Compare your calculated ΔT_c with the temperature rise given in the calorimeter report for the run. They should be in agreement to within 1-2%. If there is a larger discrepancy, Make a note of this in your ELN. Discuss with your instructors to make sure you understand why this might happen.

You have now seen how to analyze a thermogram using Logger Pro, to obtain good values of ΔT_c. For subsequent runs, choose either to use your calculated ΔT_c from the manual data workup using LoggerPro, or the Temperature Rise from the calorimeter report. Even when the two do not agree within ~1-2% of each other, using one method consistently for all runs tends to give reasonable results.

Calculation of the calorimeter heat capacity

Use the calibration data from dissolution of KCl to calculate the heat capacity of your calorimeter (C_p). Each calorimeter has a unique C_p. The C_p of your calorimeter should be a constant, provided you always use the same amount of water in each run and the temperature of the calorimeter components is constant. However, you can also calculate the heat capacity of the "empty" calorimeter (C_p') without water.

Dissolution of KCl in DI water absorbs 230.98 J/g at 25˚C. The quantity of heat absorbed on solution of KCl increases by 2.066 joules per gram for each degree drop in temperature below 25˚C. The total energy absorbed in the reaction is given by

$$q = m[-230.98\frac{J}{g} - 2.066\frac{J}{g^{\circ}C}(25^{\circ}C - T_{0.63R})] \tag{10.3.4.3}$$

where:

- $q =$ heat evolved in joules
- $m =$ mass of KCl in grams
- $T_{0.63R} =$ temperature at the $0.63R$ point on the thermogram in $^{\circ}C$.
- The term, $2.066\frac{J}{g^{\circ}C}(25 - T_{0.63R})$ adjusts the heat of reaction to any temperature above or below the 25˚C reference temperature.

To calculate C_p (in $\frac{J}{^{\circ}C}$) for your calorimeter and its contents, use the equation:

$$C_p = \frac{q}{\Delta T_c} \tag{10.3.4.4}$$

Determine the heat capacity of the empty calorimeter (C_p') by subtracting the heat capacity 100.00 g of water from the C_p.

$$C_p' = C_p - (100.00g \times C_w) \tag{10.3.4.5}$$

where:

$C_p' =$ the heat capacity of the empty calorimeter in joules per $^{\circ}C$
$C_w = 4.1796\frac{J}{g}$ is the specific heat capacity of water in joules per gram at $25^{\circ}C$
$100.00g =$ the amount of water used (density of water at $25^{\circ}C$ is 1 g/mL)

Report the value of C_p' in your ELN.

Calculate the heat of solution for each salt analyzed

The enthalpy change for a reaction conducted at constant pressure is given by the following equation, as discussed in the Introduction section:

$$\Delta H\,(T_1) = -\left[C_{p,cal} + C_{p,\text{ products}}\right](T_2 - T_1) \tag{10.3.4.6}$$

From the equation above, the $\Delta H\,(T_1)$ would be the change in enthalpy for the reaction. We can also calculate the change in enthalpy per mole of reactant using a modified form of Equation 10.3.4.6.

$$\Delta H\,(T_1) = \frac{-\left[C_{p,cal} + C_{p,\text{ products}}\right](T_2 - T_1)}{\text{moles of reactant (salt)}} \tag{10.3.4.7}$$

where:

$$C_{p,\text{ products}} = \text{volume of sol.} \times \text{density of sol.} \times \text{specific heat capacity of sol.} \tag{10.3.4.8}$$

and,

volume of sol. = total volume of reactant solution (100.00 mL, assume negligible volume change for dilute solution)

density of sol. = 1.00 gram/mL (assumed for dilute aqueous solution)

specific heat capacity of sol. = 4.18 joule/gram (assumed for dilute aqueous solution)

Therefore, we can also express Equation 10.3.4.7 as follows:

$$\Delta H\left(T_1\right)=\frac{-\left[C_{p,cal}+(\text{volume}\times\text{specific heat capacity of sol.})\right]\left(\Delta T_c\right)}{\text{moles of reactant (salt)}} \tag{10.3.4.9}$$

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10.3.5: Discussion questions

The previous section (data analysis) describes how to handle your data. You should perform the described calculations and analysis and describe them in your notebook. In addition, the following should be addressed in your notebook.

1. Perform a full propagation of errors analysis of your results and suggest possible sources of systematic error.
2. Begin your discussion with a quantitative comparison of your experimentally measured values with the literature values of the enthalpy of solution for $\mathrm{CH_3COONa}$, $\mathrm{CH_3COONa \cdot 3\,H_2O}$, and NaCl (found in the CRC handbook). Do your results agree with accepted values within your estimated uncertainty? If not, suggest possible reasons for any differences found.
3. Discuss the significance of *the sign* of ΔT_c.
4. Relate the differences in the enthalpies of solution of the two sodium acetate salts to differences in their respective lattice energies. To do this, you might begin by drawing a Hess's Law type diagram that relates the enthalpy of solution of the solids to the lattice energies and the hydration energies of the gaseous ions. Look up the lattice energy of anhydrous sodium acetate in the CRC Handbook. Note: Use the U_{pot}^{BFHC} values)
5. Use the enthalpies of solution of the two sodium acetate salts to calculate the enthalpy change for the following reaction:

$$\mathrm{CH_3COONa_{(s)} + 3\,H_2O \longrightarrow CH_3COONa \cdot 3\,H_2O_{(s)}} \tag{10.3.5.1}$$

   From your result, calculate the lattice energy of sodium acetate trihydrate. Returning to your Hess's Law diagram, use your results so far and the known gaseous ion hydration energy of $\mathrm{Na^+}$ to calculate the gaseous ion hydration energy of the acetate anion (see your instructors if you need help). Compare this with an accepted value. How well does it agree?
6. Consider now sodium chloride and potassium chloride. You have an experimental value for the enthalpy of solution of sodium chloride. In addition, you used the enthalpy of solution of potassium chloride (230.98 J/g) in the calibration of the calorimeter. Convert the enthalpy of solution of KCl to kJ/mole and compare it to the enthalpy of solution of NaCl. In discussing these results, you should do a similar calculation to what you did for the acetate salts, and calculate their respective lattice energies from your enthalpies of solution and the known gaseous ion hydration energies. In addition, you should relate the differences in lattice energies to the relative sizes of the sodium and potassium cations. What is the general trend that we would expect to see in lattice energy as it relates to the size of the ions?
7. Why is it appropriate to approximate the conditions in this experiment to infinite dilution? (see Alberty Section 2.21). Look again at the figure showing Integral Heats of Solution (Fig 6.3.1.1). In your experiments, were the sample masses that you used appropriate for an approximate measurement of the enthalpy of solution at infinite dilution? Considering the technical specifications of the calorimeter and the calorimetric thermometer, given in the Instrumentation Specifications, what is the consequence of using sample sizes small enough to yield enthalpies of solution consistent with infinite dilution?

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10.4: BOMB CALORIMETRY

10.4.1: Introduction to bomb calorimetry
10.4.2: Instrumentation and Safety
10.4.3: Experimental
10.4.4: Data analysis
10.4.5: Calculations and Discussion

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10.4.1: Introduction to bomb calorimetry

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10.4.2: Instrumentation and Safety

Instrumentation

The undergraduate teaching labs at Duke have two Parr 1341 Plain Jacket Oxygen Bomb Calorimeters (see Figure). This instrument consists of:

1. A "bomb" in which the combustion charge is burned.
2. An inner bucket holding a measured quantity of water in which the bomb is placed.
3. A calorimeter jacket in which the inner bucket is placed.
4. A calorimeter cover which holds a stirring device and precision thermistor which are, in turn, immersed in the inner bucket when the cover is placed on the calorimeter jacket.
5. A Parr 6772 Calorimetric Thermometer with a built-in ignition unit and a thermistor probe to measure the temperature rise of the water in the inner bucket during the combustion process.

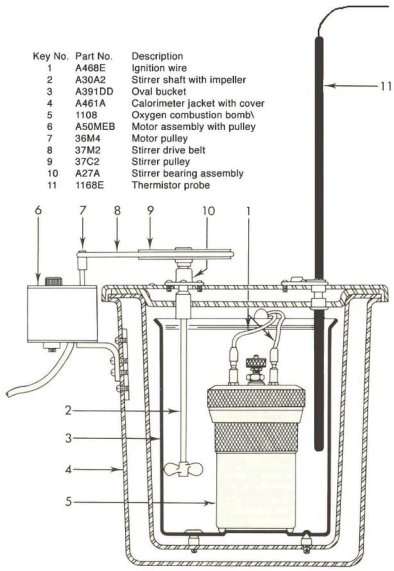


Figure 10.4.2.1: Copy and Paste Caption here. (Copyright; author via source)

Good repeatability can be obtained with the 1341 Calorimeter provided that the temperature rise and heat leak corrections are measured and applied carefully. The repeatability is 0.2% when using the Parr 6772 Calorimetric Thermometer.

Safety

Caution

The bomb should be assembled, filled with oxygen, and operated WITH EXTREME CARE following instructions from your TA.

This calorimeter and its use are described in detail in Parr Operating Instructions,[1] Matthews,[2] and Sime.[3] To ensure safe operation and optimum precision, **this experiment should be attempted only after you have become thoroughly familiar with the contents of the references cited above**. There is a danger in the operation of the bomb calorimeter both from explosion and electric shock. Operation is safe provided that the following precautions are taken:

1. There is a possibility of electric shock and of short circuit from exposed terminals and metal parts of the calorimeter, and therefore the working area must be kept completely dry.

2. The bomb must be kept clean and when dismantled should be placed on a clean folded towel or stand if provided. Be careful not to scratch, dent, or drop the bomb. It is particularly important to avoid marring the surfaces at which closure is affected and to keep these areas scrupulously clean.
3. Switch off all electricity supplies before assembling or dismantling the bomb.
4. The amount of sample should not exceed 1.0 g.
5. The pressure of oxygen must not exceed 25 atm.
6. Do not fire the submerged bomb if bubbles of gas show that it is leaking.
7. Wear a face shield while pressurizing the bomb.
8. Stand well clear of the bomb as it is fired and for at least 30 s afterwards.

References:

1. Parr Operating Instructions, "Instructions for the Parr 1341 Calorimeter," Parr Instrument Co., Moline, IL. (found in the lab or online at www.parrinst.com)
2. Matthews, G. P. Experimental Physical Chemistry, Oxford University Press, Oxford, 1985, Section 3.1.
3. Sime, R.J. Physical Chemistry. Methods, Techniques and Experiments, Saunders, Philadelphia, PA, 1990, pp. 420-431.

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10.4.3: Experimental

General Steps to prepare the materials and calorimeter assembly

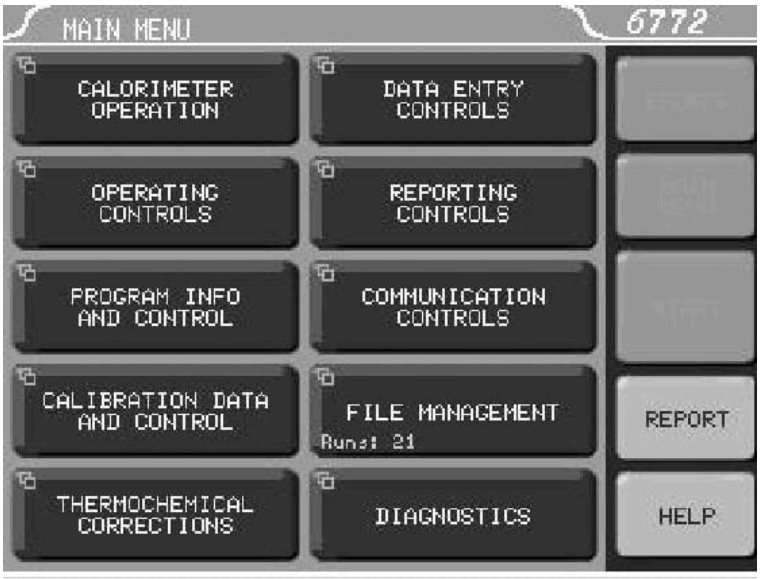
1. **Prepare room-temperature water:** Fill a 2-liter volumetric flask to the TD ("to deliver") mark with deionized water *at least* 20 minutes before each run, so that the contents are equilibrated at room temperature prior to use. There are two flasks per station. Fill both flasks at the start of the laboratory period, and after the start of each run, so that the water for subsequent runs comes to thermal equilibrium while the prior run is being performed.
   *Volumetric flasks are "Class A" glassware, and the errors associated with their measurements can be found either on the flask itself or in a table of tolerances (like this one, click).
2. **Prepare sample pellet** (See Figure 10.4.3.1A-C).
   - Weigh **approximately 0.85 g** (between $0.8000 - 0.9000$ g) of solid sample.
   - Press the sample into a pellet using the pellet press.
   - Carefully re-weigh the pellet and be sure it is between $0.8000 - 0.9000$ **g** .
3. **Bomb head:** Place the bomb head on its stand and put the ignition cup in place (See Figure 10.4.3.1D).
4. Place the weighed sample pellet in the ignition cup (See Figure 10.4.3.1D/E).
5. **Place fuse wire:** Cut about 9-10 cm of nickel chromium fuse wire ($\Delta_{T_1} = -6.876 \text{ kJ/g}$\)) and weigh it carefully. Attach the ends of the wire to the two electrodes and loop it in such a way that it rests upon the surface of the pellet. Take care that it does not come into contact with the combustion cup. Assemble the bomb carefully; the pellet and fuse wire are in fragile contact (See Figure 10.4.3.1E).

   > **Note**
   >
   > Handle the fuse wire with care. If you allow the wire to bend too sharply or to develop kinks, it will burn off at the weak point upon ignition, and combustion of the pellet will not occur. Consequently no temperature rise will be observed and you will have to disassemble the bomb and prepare a new pellet and ignition wire.

6. Your TA will supervise the assembly of the bomb and the flushing and filling of the bomb with pure oxygen (25 atm) (See Figure 10.4.3.1F-H).

   > **Caution**
   >
   > - **YOU MUST WEAR A FACE SHIELD AT ALL TIMES WHEN THE BOMB IS PRESSURIZED**.
   > - **DO NOT EXCEED 30 atm**! If you do, open the valve to release the oxygen slowly over a one minute period, dismantle the bomb and begin again.

   Prior to removing the hose from the bomb, bleed the oxygen from the connecting line so that it may be detached from the bomb safely.
7. The bomb is placed in the inner bucket (See Figure 10.4.3.1I).
8. Add 2 liters of distilled water, at room temperature. (Use a 2 L volumetric flask to measure the water and see step (1) above.)
9. Assemble the apparatus and make sure that the thermistor is immersed in the water to the same depth as the stirrer propeller (See Figure 10.4.3.1I-K).
10. Power on the **Parr Calorimetric Thermometer Unit** using the **on/off** switch at the rear left of the instrument.
    - After a short "Self Test" routine the following screen will appear.



- Press **Operating Controls**. Look over the settings; **Method of Operation** should be *Combustion*; **Reporting Units** should be *cal/g*; and, **Spiking Correction** should be *off*.

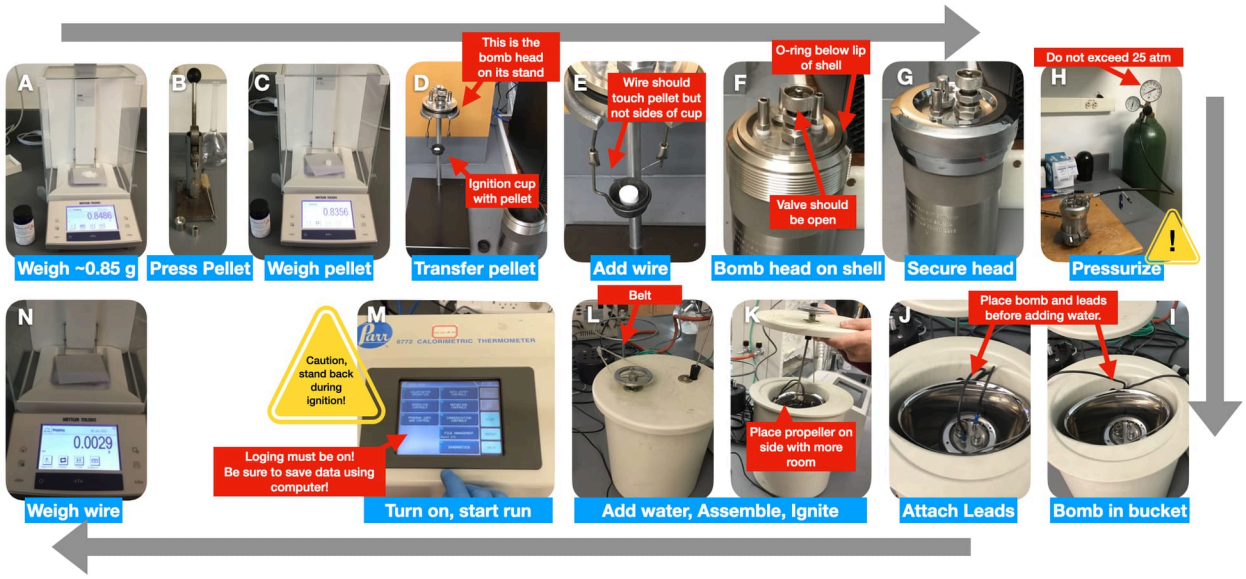


Figure 10.4.3.1: Visual overview of some of the major steps in a bomb calorimetry run. (CC-BY-SA; Kathryn Haas)

Standardization Procedure

The calorimeter is calibrated using benzoic acid ($\Delta_{T_1} = -26.436\ \mathrm{kJ/g}$). To standardize the calorimeter (measure its heat capacity), begin by following steps 1-10 above using benzoic acid as the sample. Continue with the procedure outlined below and consult your TA as necessary.

11. On the **Parr Calorimetric Thermometer Unit** screen, press **Escape** or **Main Menu** to go back to the Main Menu.
12. Press **Diagnostics**.
    - Check the settings; the **Data Logger** should be *off*. If it is on, press the **Data Logger** button to turn it *off*.
    - Press the **Delete Data Log File** button to clear the data log.
    - Check to be sure that the **Data Log Format** is set to *Data Format (csv)*.
    - **Then, turn the Data Logger back *on***.



13. Press the **Start** button on the right side of the screen.
    - The stirrer to the bomb calorimeter will turn on automatically.
    - You will be prompted to enter a Sample ID. Use the format: *initials*MMDDYY-N, where: *initials* are your initials; MMDDYY is the date in month, day and year format; and, N is the number of the run (e.g., 1 for the first benzoic acid run).

> Note
>
> **Note**: When naming files,
>
> - **First calibration run with Benzoic Acid: N=1**
> - **Second calibration run with Benzoic Acid: N=2**
> - **First run with carbohydrate: N=3**
> - **Second run with carbohydrate: N=4**

    - Press **Enter** on the calorimeter screen.
    - You will be prompted for which bomb number to use: use **1**. Press **Enter**.
    - Enter the sample pellet mass (in grams). Press **Enter** when you are done.



> **Note**
>
> At this point your data collection has started and you are logging temperature and time data.
>
> There will be a seven-minute pre-run measurement of the starting temperature, followed by ignition, and then about seven minutes post-run measurement of the final temperature. Moments before ignition, the instrument will beep loudly. **Stand back during ignition** (when you hear the beeping) in case of failure of the bomb head.

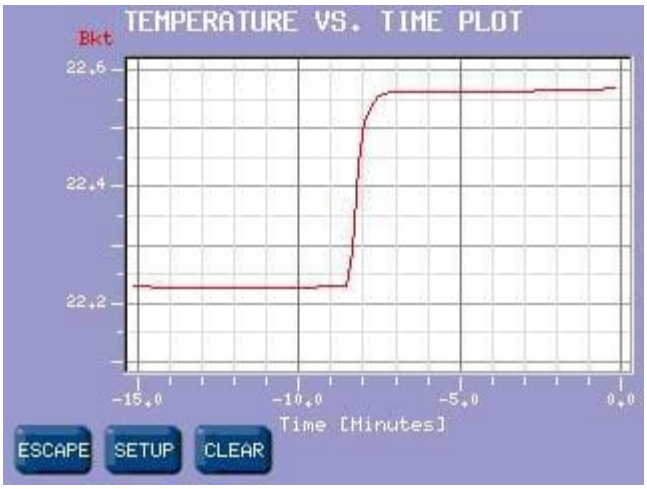
14. In the meantime (during pre-run measurement)....press the **Main Menu** button on the right side of the screen to return to the Main Menu.
15. Then press **Calorimeter Operation**. You will be taken to a screen that shows the progress of the current run. You will see your sample run information along with the temperature of the water (listed as the **Bucket Temperature)**. At the bottom of the screen you will see a timer that will monitor the progress of the run.
16. Press the **Temperature Graph** button on the calorimeter.
    - A real-time image of the temperature inside the calorimeter (the Bucket Temperature) will appear.
    - Press **Setup** and you will see the following screen.
    - Set the **Bucket Min Value** about 0.5 degrees below the pre-period baseline temperature and **Bucket Max Value** about 2.5 degrees above the pre-period baseline temperature.
    - Press **Escape** when you are done.



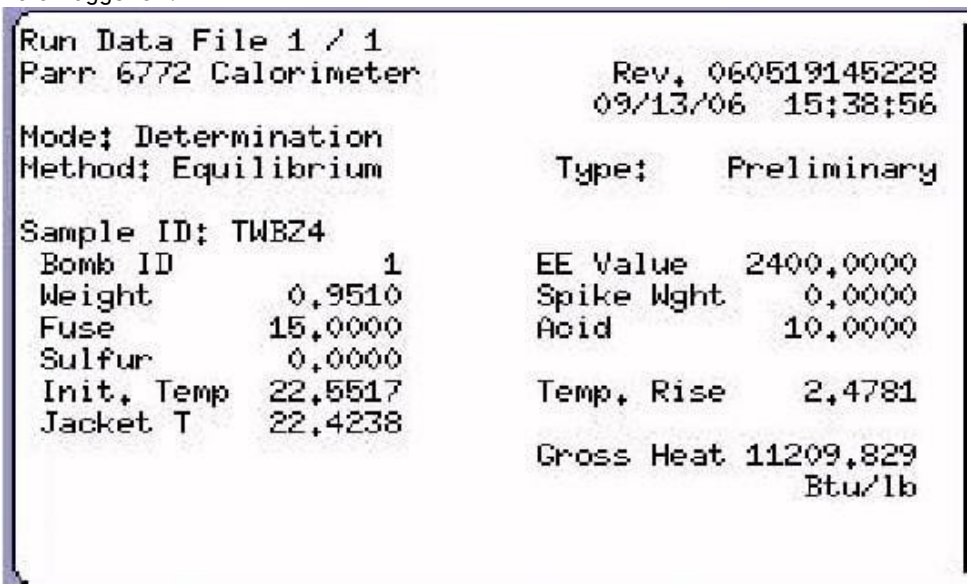
17. Go to the computer associated with the calorimeter.
    - Click the **Parr Calorimeter** shortcut found on the main Windows desktop screen. This will take you to a Web page associated with the calorimeter.
    - Click on the **LCD Image** tab; a screen shot of what is currently on the calorimeter display will appear. This is not a "living" image, but one that is captured at the moment you clicked the **LCD Image** button. To update the image press the **F5** key on the computer keyboard.



18. About seven minutes after starting the run you will hear a beep and the calorimeter will ignite the sample.
    - Stand back when you hear this beeping.
    - After ignition, you can watch the temperature rise inside the system by monitoring the **Temperature Graph** either on the calorimeter display or by updating the **LCD Image** on the computer screen.
    - Watch the display closely for the first minute or two after ignition to be sure that the sample is burning. If there is an Ignition Failure (something that happens occasionally) you will get an error message on the calorimeter screen and the run will stop. If that happens, ask your TA to supervise as you carefully remove the bomb from the calorimeter; release the oxygen pressure by opening the outlet value, open the bomb; remove the old sample and wire; and, prepare another run.



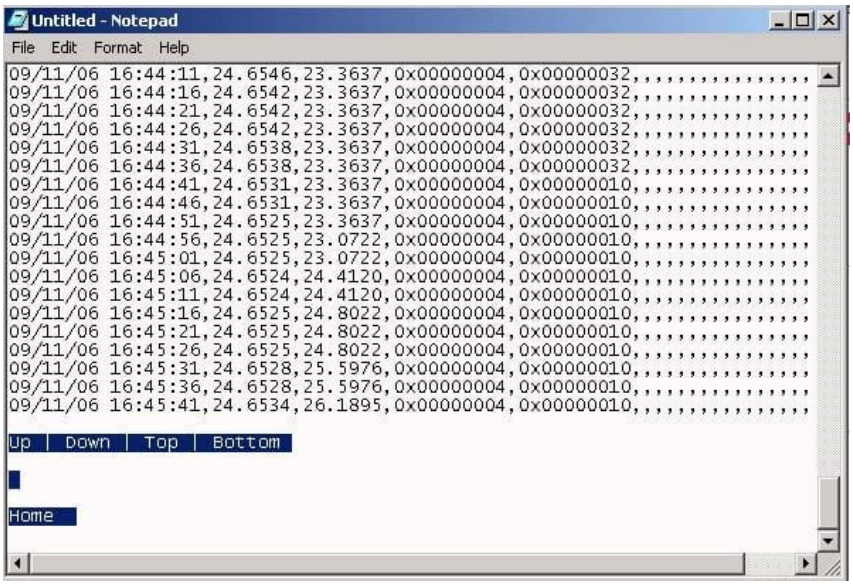
19. Near the end of the run you will hear another beep from the calorimeter telling you the run has completed.
20. Upon completion, press **F5** on the computer screen and capture the Temperature Graph on the computer screen at that moment.
    - Move the mouse toward the upper left of the computer screen and a small menu bar  will appear. Click on the **save** button and save a copy of this image to c:\data\ *initials*MMDDYYN.jpg (where N is the run number).
    - When the report for the run appears on the *Parr Calorimeter* screen press **F5** on the computer keyboard to bring an image of the report onto the computer screen. Save this image to c:\data\ *initials*MMDDYYN**rpt**.jpg (where N is the run number).
21. Press **Escape** on the *Parr Calorimeter* screen and the report will disappear, leaving the thermogram.
22. Press **Escape** again and you will return to the Calorimeter Operation Screen.
23. Press **Main Menu** on the button bar and then press the **Diagnostics** button to navigate back to the Diagnostics Screen.
24. Press the **Data Logger** button and when you get to the Data Logger screen press the new **Data Logger** Button to turn the Data Logger *off*.



25. Return to the computer screen. Click on the **Home** button at the bottom of the browser window. Then Click on the **Data Log** tab.



You will get a new window containing the logged data from the run. Each row contains the date, the time, the bucket temperature, the jacket temperature and two columns that are mostly zeros.
- Use the mouse to highlight the entire data log (it will be long and you will need to scroll down the window as you highlight).



- Select **Copy** from the **Edit** menu.
- Open the Windows **Notepad** (Start →Accessories → Notepad) and **Paste** the data log into the Notepad window. Delete any text that may appear below the last row of data.
- Select **Save As** from the **File** menu and save the Notepad file in c:\data*initials*MMDDYYN.txt.

> **Imprtant: always save the data log!**
>
> In this course, you must create and save the Notepad (.txt) files for every run in case you need to revisit the data later. Alwasy save the data log for each run using the instructions above.

26. **Ask your TA to supervise as you carefully dismantle the bomb**.
    - Open the oxygen outlet value **very slowly** to relieve the oxygen pressure.
    - Open the bomb and inspect for incomplete combustion indicated by traces of soot.
    - The inside should be clean but covered with a dew-like layer of water.
    - If there is evidence of incomplete combustion (sample remaining after combustion), the run must be re-done.
    - If you find unburned wire it should be removed and weighed; Subtract the mass of unburt wire from the original mass of fuse wire to determine the actual mass of wire burned.
27. Carefully clean and dry the apparatus.
28. Repeat with another benzoic acid sample.

Determination of the Average Heat of Combustion of a Carbohydrate

1. Repeat the above experiment twice, substituting the sugar for the benzoic acid. You should clean any benzoic acid off of the pellet press with a bottle brush before making a pellet with sugar.
2. Carefully clean and dry the apparatus after each use.

Shut down and cleanup

After you have collected two replicate datasets for the calibration and two replicate datasets for carbohydrate, please clean the instrument and workstations and prepare for the next person to use the instrument:

- Clean and dry all components of the bomb and calorimeter. The bomb head should be on its stand with valve open, the inside of the bomb should be wiped with a paper towel to remove water.
- Power off the instrument using the switch in the back.
- Turn the oxygen tank completely off (ask your TA to supervise).
- Wipe the bench area and sink where you were working.
- Use the brushes (looks like a small paint brush) to gently remove any residue or powder from the inside and outside of the

balance, then wipe the bench around the balance.

Before you leave, go through all the steps of data analysis with logger pro and discuss the correction for non-adiabaticity with your TA. Use the rest of lab time to make progress on the data and error analysis so that your TA is available to answer any questions that come up.

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10.4.4: Data analysis

Calculation of ΔT_c from the thermogram using Logger Pro

You will use **Logger Pro** software to analyze at least one thermogram collected during the experiment. Logger pro is available on computers in the P-chem lab, and is also available from Duke OIT. However, versions later than 3.8.6 have trouble importing the .txt data files from the calorimeter. If you would like version 3.8.6 for your own computer, it is available on the course Sakai site.

The graph of temperature (T) versus time (t) produced in this experiment is called a thermogram and should resemble that shown in Figure $10.4.4.1$. Because the initial (pre-period) and final (post period) slopes of the thermogram may be different, and because the temperature rise due to a chemical reaction is usually nonlinear, it is necessary to decide on a procedure to best estimate the true net temperature rise in the experiment. A common method is to extrapolate the post period slope backward in time and the pre-period slope forward in time (the dotted lines in Figure $10.4.4.1$).

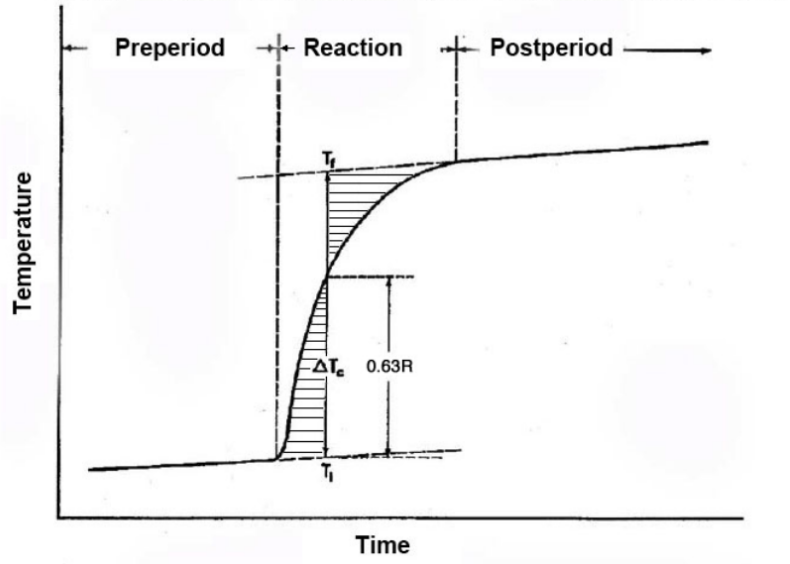
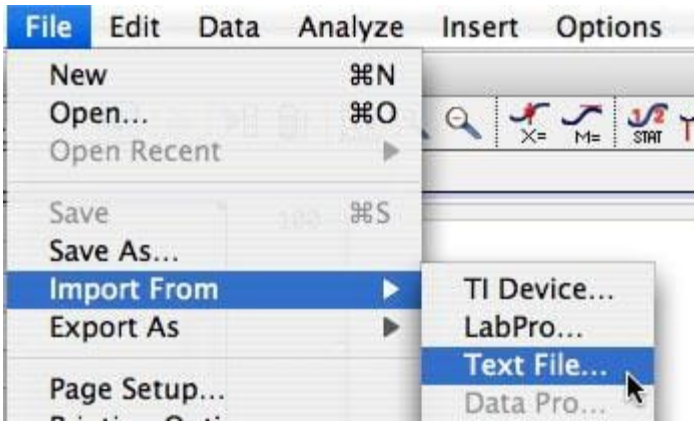


Figure $10.4.4.1$: ypical Temperature Rise Curve for 6755 Calorimeter. (Duke Chem)

The net temperature rise (ΔT_c) can be measured from the difference of these two extrapolated lines at some intermediate time in the reaction period. The exact location of this intermediate time depends on the calorimeter, and on the reaction being studied. A frequently used criterion for estimating this time is to measure ΔT_c at the point where the shaded areas in Figure 4 are equal. The temperature rise from the reaction increases exponentially with time, as $T = T_i + A(1 - e^{-kt})$, where A is the temperature rise (ΔT_c) and k is a constant. It can be shown that these two shaded areas will be equal when $t = \frac{1}{k}$, or when the temperature increase is approximately $0.63\Delta T_c$. This procedure usually works well for chemical reactions of the type studied here. A procedure for graphical analysis for determination of ΔT_c based upon this criterion is outlined below.

1. Start Logger Pro by Clicking on the  icon on the computer main screen. When the program loads, you will see a *Data Set* window on the left side of the screen and a *Graph* window on the right. Click once in the Graph window and then select **Graph Options** from the **Options** menu. Be sure that *Connect Points* is **not** checked. The *Point Protectors* option should be checked.

2. Select **Import From – Text File** from the **File** menu. When prompted, select your Windows Notepad (.txt) file for your first KCl run. The data will import directly into the *Data Set* window and the thermogram will appear in the *Graph* window.

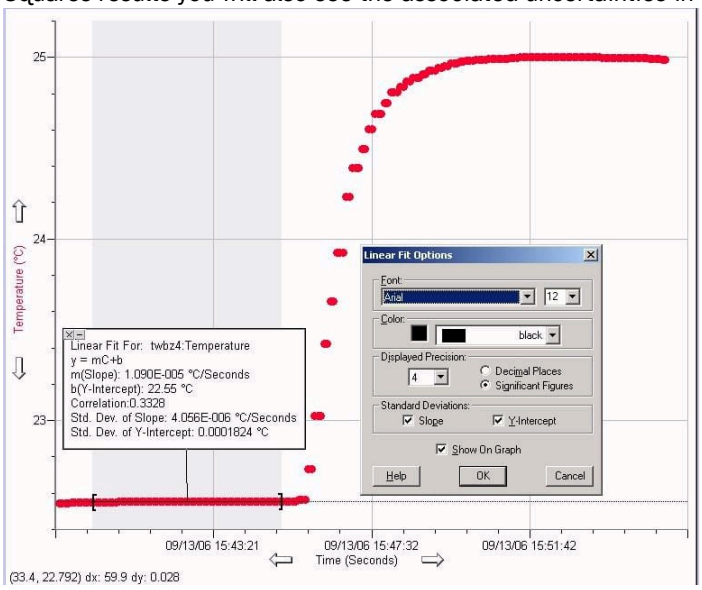


3. Look first at the *Data Set* window. Double Click on the **Column** heading above the first column of numbers. A dialog box will appear and you can change the name of the column from Column to **Time**. In the Units box enter **Seconds**. Repeat this procedure for Column 2 – changing it to **Temperature**. There is a Symbols entry box below the Units section where you will find the degree symbol so that you can enter $^{\circ}C$ for the units of the Temperature axis.

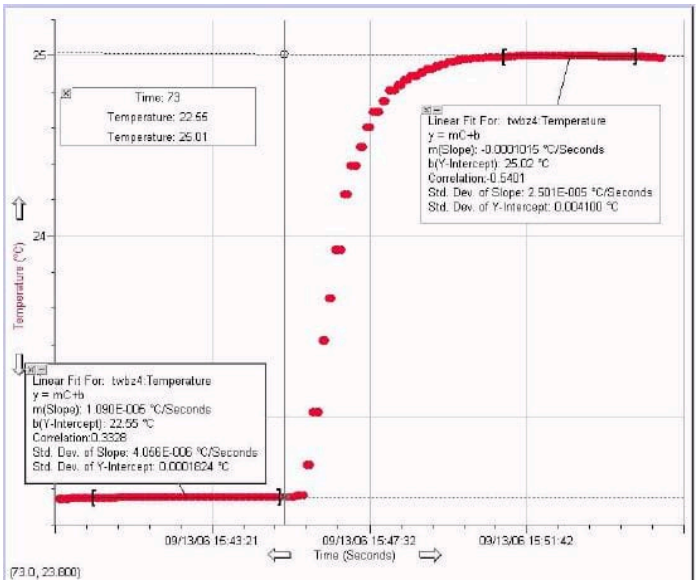


4. Look now at the pre-period baseline. From within the Graph window, use the mouse to click and drag along a section of the pre-period baseline that accurately reflects the slope of this portion of the thermogram. The software will highlight the selected portion of the baseline. Click on the 

button in the button bar at the top of the screen. A Linear Least-Squares line will be calculated for the selected data. The results will be shown in a text box inside the graph window. You can move the text box to any position in the graph window with your mouse. Double-click inside this text box and an **Options** box will appear. Put checks in the **Slope** and **Intercept Standard Deviations** boxes and click **OK**. Now when you look at the Least-Squares results you will also see the associated uncertainties in slope and intercept.



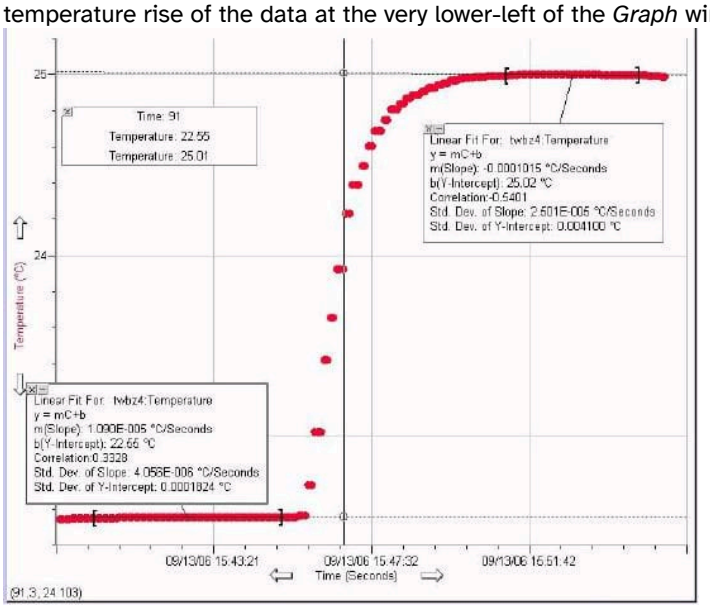
5. Repeat step 4 procedure for the *post-period* baseline.



6. The Interpolate function in Logger Pro will be useful to find R and ΔT_c. To begin, Select **Interpolate** from the **Analyze** menu. A vertical bar running between the pre- and post-period Linear Least-Squares lines will now move with your cursor. In addition, a new text box appears which will show you the temperature of the pre- and post-period lines at the position of the bar.
7. Move the interpolation bar to a point close to the beginning of the reaction period (see the picture above and also Figure $10.4.4.1$). Calculate R at this point by subtracting the final interpolated temperature from the initial interpolated temperature. In the picture above $R = 25.01–22.55 = 2.46^{\circ}C$. Multiply R by 0.63 and add this result to the initial interpolated temperature. In the example above:

$$T_{0.63R} = 22.55 + (0.63(2.46)) = 24.0998 \approx 24.10^{\circ}C \tag{10.4.4.1}$$

8. Move the Interpolation bar to the point where this temperature, $T_{0.63R}$, intersects with the thermogram. You can follow the temperature rise of the data at the very lower-left of the *Graph* window.



9. Read the initial temperature (T_i) and the final temperature (T_f) at the points of intersection of this line with the pre- and post-period lines and subtract these to determine the corrected temperature rise (ΔT_c due to the combustion of the sample and the burning of the fuse wire:

$$\Delta T_c = T_f–T_i \tag{10.4.4.2}$$

10. Compare your calculated ΔT_c with the temperature rise given in the calorimeter report for the run. They should be in

agreement to within a couple hundredths of a degree. If there is a larger discrepancy, look carefully at your thermogram to be sure your pre- and post-period line accurately reflect the baseline behavior of the system before and after the run. You can make adjustments to the Linear Least-Squares line simply by moving the brackets that enclose the selected data. Check also to be sure that your *Interpolate* line is correctly positioned.

You have now seen how to analyze a thermogram using Logger Pro, to obtain values of ΔT_c; this value should be in good agreement with the reported Temperature Rise from the calorimeter. For subsequent runs, choose either to use your calculated ΔT_c from the manual data workup using LoggerPro, or the automatically corrected Temperature Rise from the calorimeter report. Even when the two do not agree within ~1-2% of each other, using one method consistently for all runs tends to give reasonable results.

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10.4.5: Calculations and Discussion

Please show work and/or address the following questions in your notebook. For all quantitative values, show propagation of error and report values ± error appropriately.

Calculations

1. **Calculate the Calorimeter heat capacity:**
   Use the calibration data from combustion of benzoic acid to calculate the heat capacity of your calorimeter (C_v) in kJ (including bomb and contents, bucket, immersed portion of the thermometer) using Equation 10.4.5.1. Each calorimeter has a unique C_v. The C_v of your calorimeter should be a constant, provided you always use the same amount of water in each run and the temperature of the calorimeter components is constant. Hint: Use ΔU_{T_1} for benzoic acid and solve for $C_{v,cal}$.

$$\Delta U_{T_1} = m\left(26.436\ \frac{kJ}{g}\right) + m'\left(6.876\ \frac{kJ}{g}\right) = -\Delta T_c\left(C_{v,cal} + m''(C_{H_2O})\right) \tag{10.4.5.1}$$

   where
   - $C_{H_2O} = 0.00418 \frac{kJ}{deg\ g}$ (heat capacity of water)
   - m = mass of benzoic acid used
   - m' = mass of nickel chromium fuse wire used
   - m" = mass of water in the bucket
   - ΔT_c = corrected temperature rise
   - $-26.436 \frac{kJ}{g}$ = heat of combustion of benzoic acid
   - $-6.876 \frac{kJ}{g}$ = heat of combustion of nickel chromium wire
2. Calculate the ΔU_{T_1} of the carbohydrate:
   Use Equation 10.4.5.2 to calculate the energy released from combustion of the carbohydrate.

$$\Delta U_{T_1} = -\left[\frac{\left[C_{v,cal} + m''\left(C_{H_2O}\right)\right]\Delta T_c - 6.876 \frac{kJ}{g}\ m'}{M}\right] \tag{10.4.5.2}$$

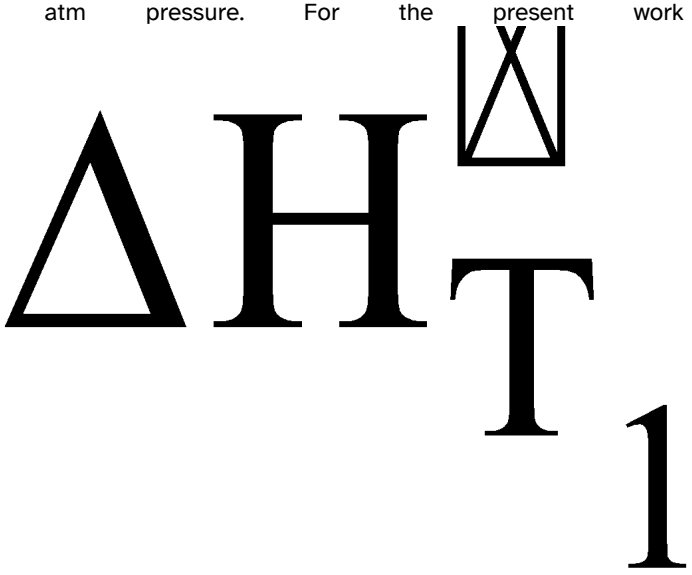
   where M is the mass of carbohydrate sample used.
3. Calculate heat of combustion at constant pressure, ΔH_{298}. (See introduction to calorimetry section and consider how heat and enthalpy are related when pressure is constant). Compare your result with the literature value (The CRC handbook has a table of heats of combustion).
4. Draw the structure of the sugar and write a balanced chemical equation for combustion of the sugar in oxygen.
5. Using the molecular weight and empirical formula of the sugar, calculate the heat of combustion in units of kJ/mol



   at constant pressure ( ), at T1 =

298 K (see Introduction section or the Enthalpy section in Atkins). Compare your result with the literature value (The CRC handbook has a table of heats of combustion).

6. Using standard enthalpies of formation for CO_2 gas (–393.5 kJ/mol) and H_2O gas (–285.83 kJ/mol) and your experimental value for the enthalpy of combustion (ΔH_{T1}), calculate the standard enthalpy of formation of the sugar at 25˚C and 1 atm pressure. For the present work the difference between ΔH_{T1} and



may be neglected.1

Discussion Questions

7. Discuss possible sources of uncertainty in this experiment,[1] and perform a complete propagation of error analysis.
8. Ask your lab partner for the identity of, and heat of combustion (ΔH_{T_1}) of their carbohydrate. **If there is no other student doing this experiment, your TA will give you data for carbohydrate different than yours.
    - In your notebook, compare the carbohydrate you used to that of your partner. Note how the two carbohydrates differ in the ΔH_{T_1} and the chemical structure.
    - Using the chemical structure of each sugar, give a rational explanation for the differences in ΔH_{T_1}.
9. At high temperatures in the presence of nitrogen gas (N_2) oxygen gas (O_2), and water, nitric acid can form. This is why the bomb must be flushed with oxygen gas prior to pressurizing it. If residual air were present in the bomb, nitric acid would be formed during combustion; thus the measured temperature rise would be a result of combustion and the oxidation of (N_2).[2] Explain how could you experimentally could determine if nitric acid was formed, and then how you could correct for the temperature rise due to formation of nitric acid.

References

1. Matthews, G. P. Experimental Physical Chemistry, Oxford University Press, Oxford, 1985, Section 3.1.
2. Atkins, P. W. Physical Chemistry, 6th Edition, W.H. Freeman and Co., New York, NY, 1997, Chapter 2. (Libretexts Textmap here)

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11: KINETICS

11.1: Pre-lab Assignment
11.2: Introduction
11.3: Experimental
11.4: Treatment of Data
11.5: Discussion
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11.1: Pre-lab Assignment

Please complete the general pre-lab assignment.

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11.2: Introduction

Kinetics

Chemical kinetics is the study of rates of chemical processes. Kinetic studies include investigation of how different experimental conditions influence the rate of a chemical reaction. The data derived from a kinetic study can give insight into a reaction's mechanism, the nature of its transition states, and can be used to construct of mathematical models that describe the reaction.

Biochemical reactions take place in aqueous media where they are catalyzed by protein molecules, called enzymes. Enzymes, like all proteins, are polypeptide polymers made up of successive α-amino acid residues. Although twenty different types of amino acids are used, the resultant polypeptide chain may contain hundreds or even thousands of amino acid residues. Each type of enzyme (or protein) is a unique chemical species having a fixed number of specific amino acids arranged in a particular sequence along the chain(s).

The catalytic activity of an enzyme depends upon the fact that in aqueous solution each enzyme assumes a particular three-dimensional structure (the native tertiary or quaternary structure) containing an "active site". The reactant molecules (usually small organic molecule) is bound in the active site, where a specific chemical reaction is catalyzed to form products.

An enzyme loses its catalytic ability if it is denatured (unfolded from its native state). Enzymes can be denatured by a change in pH, by the addition of denaturing agents such as detergents, urea, or guanidine hydrochloride, or, in some cases, by raising the temperature. Some catalytic activity may also be lost if a competing substrate, or inhibitor, is added to the solution along with the desired substrate. Many enzyme-catalyzed reactions proceed via a mechanism that can be kinetically analyzed using a formalism developed by Michaelis and Menton.

The Michaelis-Menton Mechanism for Enzyme-Catalyzed Reactions

The Michaelis-Menton treatment assumes that the enzyme (E) first reacts with the substrate (S) to form the enzyme-substrate complex (ES) which breaks down in a second step to give free enzyme and products (P).

$$\mathrm{E} + \mathrm{S} \underset{\mathrm{k_{-1}}}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{ES} \tag{11.2.1}$$

$$\mathrm{ES} \xrightarrow{\mathrm{k_2}} \mathrm{P} \tag{11.2.2}$$

Steady state hypothesis

The rate of formation of ES from E + P is very small and may be neglected. If the concentration of the complex ES is assumed to achieve a steady state

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}] = 0$$

then

$$[\mathrm{ES}] = \frac{k_1[\mathrm{E}][\mathrm{S}]}{k_{-1} + k_2} \tag{11.2.3}$$

In general, we would know the *initial* concentration, $[\mathrm{E}_o]$, of enzyme before the enzyme-substrate complex is formed, but not $[\mathrm{ES}]$ or $[\mathrm{E}]$ *after* the reaction is underway. But we can use mass balance to know that the total enzyme is equal to free enzyme plus enzyme in the ES complex. And, since the total enzyme is the same as the initial amount of enzyme:

$$[\mathrm{E}_0] = [\mathrm{ES}] + [\mathrm{E}] \tag{11.2.4}$$

We can substitute $[\mathrm{E}] = [\mathrm{E}_0] - [\mathrm{ES}]$ from 11.2.4 into 11.2.3 to get the equation in terms of initial concentration of enzyme:

$$[ES] = \frac{k_1}{k_{-1} + k_2}[\ \mathrm{S}]\ ([\mathrm{E_0}] - [\mathrm{ES}]) \tag{11.2.5}$$

Now 11.2.5 is simplified to yield an expression that to gives $[\mathrm{ES}]$ in in terms of $[\mathrm{E_0}]$:

$$[\mathrm{ES}] = \frac{k_1[\ \mathrm{S}]\ [\mathrm{E_0}]}{(k_{-1} + k_2) + k_1[\ \mathrm{S}]} \tag{11.2.6}$$

Finding the initial rate, V_0

The rate (V) of the reaction can be be expressed as the rate of formation of product with respect to time (see Equation 11.2.2). The formation of product is related to the disappearance of the ES complex and the rate constant k_2. We can express the rate of formation of products using Equation 11.2.7:

$$V_0 = \left(\frac{d[\mathrm{P}]}{dt}\right) = k_2[\mathrm{ES}] \tag{11.2.7}$$

We can apply the steady state hypothesis by substituting Equation 11.2.6 for $[ES]$ in Equation 11.2.7. This allows us to express the initial rate, in terms of $\mathrm{E_0}$:

$$V_0 = \frac{d[\mathrm{P}]}{dt} = k_2[ES] = \frac{k_1 k_2\ [E_o]\ [\mathrm{S}]}{(k_{-1} + k_2) + k_1[\mathrm{S}]} \tag{11.2.8}$$

This relation is usually rewritten in a modified form by dividing numerator and denominator by k_1 and introducing a new constant, known as the **Michaelis constant (K_M):**

$$K_M = \frac{(k_{-1} + k_2)}{k_1} \tag{11.2.9}$$

Thus, the Michaelis-Menton rate law is given by Equation 11.2.10.

$$V = \frac{k_2\ [E_o]\ [\mathrm{S}]}{K_M + [\mathrm{S}]} \tag{11.2.10}$$

Notice that if we determine the initial rate of reaction, both $[\mathrm{E_0}]$ and $[\mathrm{S}]$ are the known initial concentrations, so that 11.2.10 expresses the rate in terms of known concentrations.

Finding maximum velocity, V_{max}

Next, we examine some of the implications of the Michaelis-Menton rate law.

Recall Equation 11.2.3. That equation can be rearranged to show that K_M is an equilibrium constant:

$$K_M = \frac{k_{-1} + k_2}{k_1} = \frac{[\mathrm{E}][\mathrm{S}]}{[\mathrm{ES}]} \tag{11.2.11}$$

We see that K_M is an apparent dissociation constant of the complex ($\mathrm{ES} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{E} + \mathrm{S}$). However, from Equation 11.2.1, we can see that the true dissociation constant is $K_D = \frac{k_{-1}}{k_1}$. The $K_M = K_D$ only if $k_2 << k_{-1}$. This equality will be valid when most of the complex dissociates to $\mathrm{E} + \mathrm{S}$ rather than reacting to form product; that is to say, the initial reactants E and S are basically in equilibrium with the complex ES.

When the concentration of substrate (reactant) is so large that it pushes the equilibrium of Equation 11.2.1 ($\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES}$) far to the right, essentially all of the enzyme is in the form of the complex. Under these conditions, the reaction proceeds at its maximum rate:

$$\text{Max. Rate } = \mathrm{V_{max}} = k_2\ [\mathrm{E_0}] \quad \text{ when } [\mathrm{S}] >> K_M \tag{11.2.12}$$

Under these conditions, increasing $[\mathrm{S}]$ does not affect the reaction rate.

On the other hand, when the substrate concentration is small enough that $[\mathrm{S}] < K_M$, then the rate varies linearly with substrate concentration and the rate can be expressed as:

$$\mathrm{V} = \frac{k_2\,[\mathrm{E}_0]\,[\mathrm{S}]}{k_\mathrm{M}} \quad \text{when } [\mathrm{S}] < K_M \tag{11.2.13}$$

Hence, the reaction rate depends upon substrate concentration in the manner shown in Figure 11.2.1.

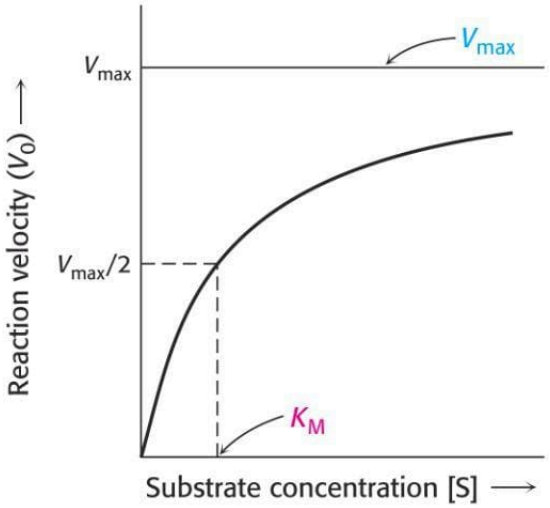


Figure 11.2.1: Variation of Reaction Velocity with Substrate Concentration According to the Michaelis-Menton Model

If we substitute $V_{max} = k_2[\mathrm{E}_0]$ in 11.2.10 we obtain the following form of the **Michaelis-Menten equation**.

$$\mathrm{V} = \frac{\mathrm{V}_{\max}[\mathrm{S}]}{K_M + [\mathrm{S}]} \tag{11.2.14}$$

This equation is important because it accurately reproduces the velocity as a function of substrate concentration behavior observed for enzyme systems. Additionally, if one measures V as a function of substrate concentration it is possible to obtain values for K_M and \)(V_{max}\).

Extensions of Michaelis-Menton:

Lineweaver-Burk

We might also take the reciprocal of 11.2.14;

$$\frac{1}{V} = \frac{K_M}{V_{\max}}\left(\frac{1}{\mathrm{S}}\right) + \frac{1}{V_{\max}} \tag{11.2.15}$$

This equation has the form of a straight line and is the basis for the **Lineweaver-Burk plot,** an example of which appears in Figure 11.2.2. If the enzyme concentration, pH, and temperature are held constant, then a plot of $\frac{1}{[V]}$ vs. $\frac{1}{[\mathrm{S}]}$ for different substrate concentrations should yield a line having an intercept at $\frac{1}{V_{max}}$ and a slope of $\frac{K_M}{V_{max}}$. Knowing V_{max} and E_0 we can calculate k_2 from 11.2.12.

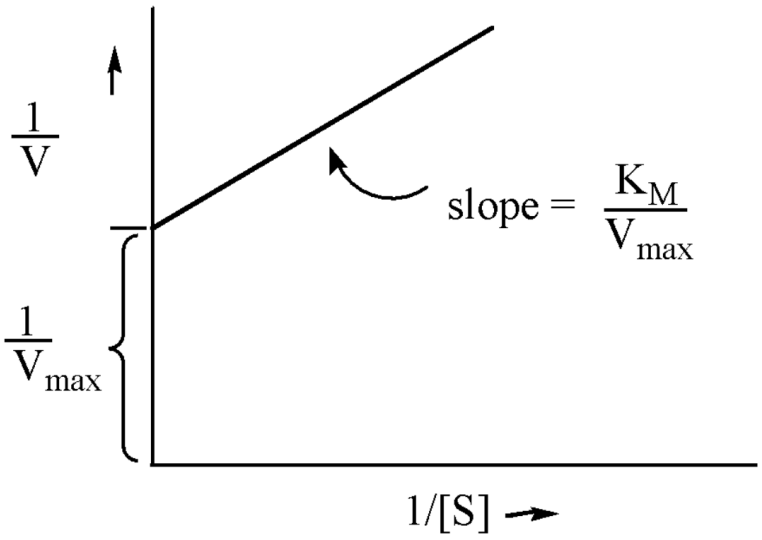


Figure 11.2.2: CLineweaver-Burk plot.

Related methods for treatment of data include the **Hanes-Wolf** plot and the Eadie-Hoftstee plot.

Hanes-Wolf

The equation of the Hanes-Wolf plot is obtained by multiplication of 11.2.15 by [S]) and giving:

$$\frac{[\mathrm{S}]}{\mathrm{V}}=\frac{k_{\mathrm{M}}}{\mathrm{V}_{\max}}+\frac{[\mathrm{S}]}{\mathrm{V}_{\max}} \tag{11.2.16}$$

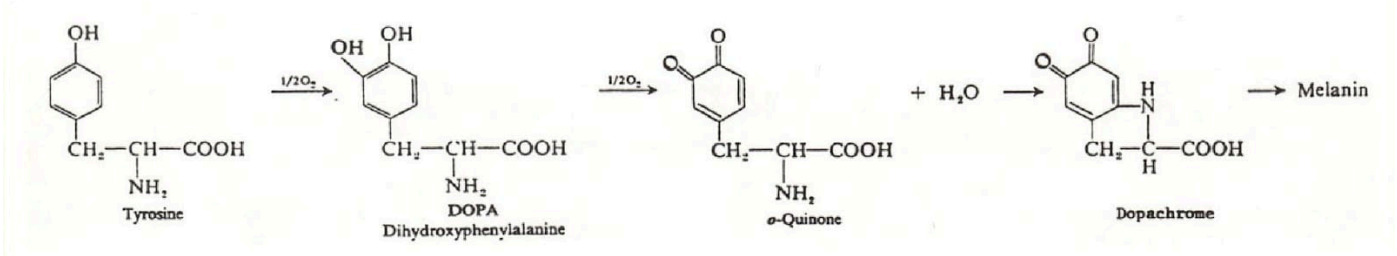
Eadie-Hofstee

The equation for the Eadie-Hofstee plot is found by multiplication of 11.2.15 by V_{max}:

$$\mathrm{V}=\mathrm{V}_{\max}-k_{\mathrm{M}}\frac{\mathrm{V}}{[\mathrm{S}]} \tag{11.2.17}$$

Tyrosinase Enzyme

The copper-containing enzyme tyrosinase (found in plant and animal tissues) consists of four identical subunits, each of molecular weight 32,000. This enzyme catalyzes the oxidation of the α-amino acid, L-tyrosine, via a number of intermediates to a dark colored polyphenolic compound, melanin:



The first step is the oxidation of tyrosine to form L-DOPA (3,4-dihydroxyphenylalanine). This step occurs slowly in the presence of tyrosinase, and is autocatalyzed by the product, L-DOPA.

The second step is the enzyme-mediated oxidation of L-DOPA. This step proceeds in a fashion that is more typical of enzymes and in a manner consistent with the kinetic models described above.[1] Quinone spontaneously reacts to form Dopachrome.

The reaction of L-DOPA (second step above) can be measured by monitoring either the concentration the reactant (L-DOPA) or the formation products. We can monitor concentrations of these species spectrophotometrically using UV-visible light because tthe absorbance of light is related to concentration by the Lambert-Beer law :

$$\text{Transmittance } = \mathrm{I}/\mathrm{I}_0 = 10^{-\varepsilon c \ell} \tag{11.2.18}$$

Where

I = intensity of light transmitted through the sample

I_0 = intensity of the incident light

ε= molar absorptivity of the absorbing species

ℓ = path length of light through the sample

c = concentration of adsorbing species

The Beer-Lambert law may also be written as

$$A = \varepsilon c \ell \tag{11.2.19}$$

Where

$A = \log(\mathrm{I}_0/\mathrm{I}) = -log(\text{ Transmittance })$

A = absorbance of the solution at a specific wavelength.

If multiple species (eg species 1, 2, and 3) all absorb at the specific wavelength measured, then the absorbance is equal to the sum of absorbance from each species (eg: A=A1+A2+A3).

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11.3: Experimental

In this lab excecise, you will monitor the the oxidation of L-DOPA catalyzed by tyrosinase.

Materials:

Chemicals: You will be provided with the following stock solutions.

1. pH 6.5 phosphate buffer prepared as follows: Weigh 6.8000 g KH_2PO_4 into a 1 L volumetric flask and add 500 ml of deionized water to dissolve. Add 139.0 ml of 0.1 M NaOH and make up to the mark with deionized water.
2. Solution of L-DOPA in buffer (5.0±0.1 mg/50.00±0.06 ml) (M.W. of L-DOPA = 197.19 a.m.u.).
3. Solution of tyrosinase in buffer (150,000 units/liter). The activity of tyrosinase is listed on the flask. The molecular weight of tyrosinase is 128,000 a.m.u.

NOTE: These are ideal concentrations; your actual stock solutions will be close but not identical to these values. You must get the actual concentrations from the flasks containing the stock solutions BEFORE performing any calculations.

Instruments: You will use two types of UV-vis spectrometers in this module.

1. Full-spectrum UV-visible spectrometer: Cary 60 or Cary 100 spectrometer
2. Single-wavelength spectrometer: A Thermo Genesys 20 spectrometer. (Instructions are linked here.)

Sample Cell: You will use a standard 1-cm cuvettes. For the full-spectum scan, you will use quartz cuvettes. For the rest of the experiment we prefer that you use *glass* cuvettes when possible (glass is optically transparent to visible light, but not UV light).

Policy on use of Cuvettes

The glass and quartz cuvettes are *expensive and fagile*. You will treat them carefully and follow the policy below so that these precious tools do not become damaged.

- At all times, **cuvettes should be held in a rack at least 12 inches away from the edge of a bench**. Never place a cuvette directly on the bench.
- When pipetting, the cuvette is held at eye level so that the user can see that they are not damaging the cuvette with the pipette tip.

Procedure:

I. Range-Finding: Determination of an appropriate wavelength for monitoring the reaction

Before you set out on a kinetics study, you must decide which wavelength (\ \Lambda\) you will use to monitor the reaction. To do this, you will scan the entire UV-visible light range using a spectrometer and determine the best wavelength to use. The ideal wavelength will be one where only one species is absorbing at the maximum wavelength of either the reactant or product. Further, it is ideal that the wavelength is in the visible range if possible, so that you can use glass cuvettes for the remaiing steps. If you determine that the ideal wavelength is in the UV range, then you must use the quartz cuvettes (which are more expensive and fragile!).

1. **Create the following solutions:** (if you have three quartz cuvettes, you can carefully mix the solutions directly in the cuvettes)
    A. REACTANT: 1.71 ml L-DOPA and 1.29 ml buffer.
    B. ENZYME: 1.29 ml tyrosinase and 1.71 ml buffer.
    C. PRODUCT: 2.00 ml L-DOPA and 1.50 ml tyrosinase.*

**This solution will produce dopachrome. The molar absorptivity (ε) of dopachrome at the peak maximum of the visible band is $3500 \mathrm{M}^{-1} \mathrm{cm}^{-1}$.*[2]

2. Calibrate the Cary spectrophotometer using the validate software and the appropriate wavelength accuracy test for your instrument (either deuterium emission or xenon emission).
3. Examine the absorption spectra, and choose a wavelength that will allow you to measure either the disappearance of substrate or the appearance of product without interference from the other components.

II. Collection of Kinetic Data

TABLE 1: Combine the DOPA, BUFFER, and TYROSINASE in that order to make solutions A,B,C,D.

Solution	DOPA, mL	Buffer, mL	Tyrosinase, mL
A	0.50	1.50	1.00
B	0.70	1.30	1.00
C	1.00	1.00	1.00
D	2.00	0	1.00

Table 1 gives the reaction conditions for the assay you will perform in this experiment.

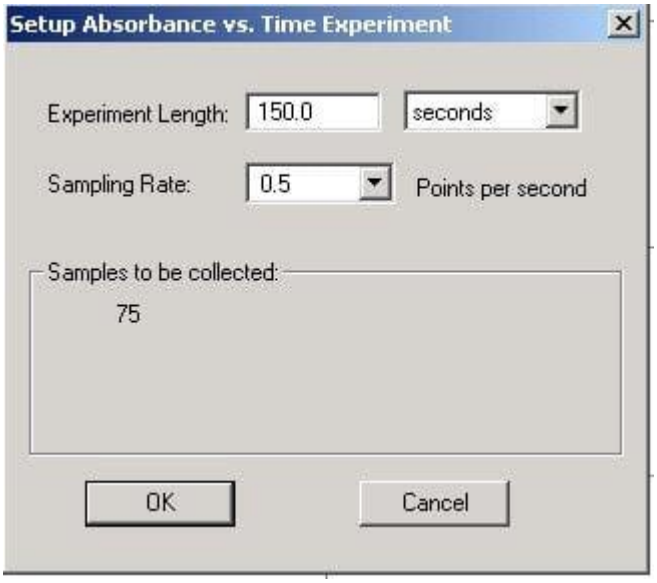
1. Turn on the Genesys 20 and let warm up for ca. 15 minutes. Set the wavelength to the value determined from the results of the range-finding part of the experiment.



- Start Spectra Pro on the computer by clicking the icon. The main screen appears.
- Notice the buttons: 

- Notice that the software recognizes the instrument and puts the name (20 Genesys) in the button bar. See your TA or the lab manager if this is not true in your case.

3. Click on the A vs Time button. Read the Experiment Notes box and then click OK.



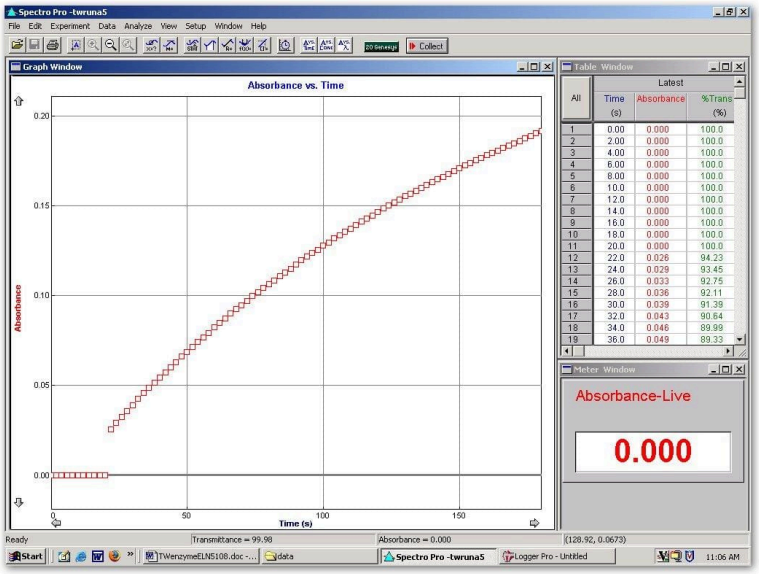
4. The Setup box appears: The Experiment Length should be 150 seconds, and the Sampling Rate should be 0.5 points per second. Click OK
5. A Calibration screen appears. Fill a clean *glass* cuvette with buffer. Wipe any fingerprints off the clear (i.e. not frosted)

windows of the surface. Insert the cuvette into the Genesys with the light path going through the clear windows; close the cover. Press the 

button on the 20 Genesys to zero the instrument. Click Done in Spectra Pro. Remove the “blank” cuvette from the instrument and set it aside for later use. (NOTE: these cuvettes cost ca. $100 each; please handle them with care and respect.)

6. Add the appropriate amounts of Buffer and DOPA to another clean glass cuvette (see Table 1). Again insert the “blank” cuvette (containing only buffer) into the instrument to check the zero (absorbance should read 0.000). Re-zero the instrument if necessary.
7. Open the cover of the instrument. Click the 

button in the Spectra Pro software. Draw up 1.00 mL of the enzyme solution. In a smooth, efficient but not rushed manner, add the enzyme to the cuvette. Draw the reaction mixture up into the pipet tip two or three times to thoroughly mix the contents. Wipe any fingerprints off the clear (i.e. not frosted) windows of the cuvette surface. Place the cuvette into the instrument with the light path going through the clear windows. Close the cover. (NOTE: Step 6 should be accomplished within ca. 15 – 20 seconds.)
8. Let the data collection run until finished. During the run you should see a smooth increase in absorbance similar to that shown here:



Notice that there is always a “Live” readout of the absorbance in the box at the lower right of the screen, and that the graph and data table is generated in real-time during the run. Notice also that in the run shown here, the first 20 seconds of the run has zero absorbance. This is the time it took to add the enzyme, mix the contents and insert the cuvette into the instrument.

8. Save the data in the data directory (c:\data) as YOURINITIALS-runLN.sbl.

> **Note**
>
> NOTE: The use of **LN** indicates that data are being stored for solution L (where L = solutions A, B, C and D), and run N (where N = 1 or 2). Choose Export Data from the File menu and save a .txt copy of the data, using the same root filename (i.e., runLNX.txt). This file should also be saved in the data directory.

9. Repeat steps 5 through 9 for runs B, C and D. Then repeat the entire sequence of runs A – D again to have two replicate runs for each substrate concentration used in the assay. (NOTE: The runs are done in the order A – D for the first trial, followed by A – D for the second trial. This order is not random; why do we do it this way?)

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11.4: Treatment of Data

Important

Do the data analysis in the lab before you leave for the day so that your TA can help you. If you use Logger Pro to do your analysis, use the lab computers which have a specific version of LoggerPro that can read the .txt files created from your data collection.

The data from this experiment can be displayed using either Logger Pro or MatLab software. In either case, you will need to have the .txt files exported for each of the experimental runs.

- There is a MatLab live script file available here (click and login with Duke credentials).
- The instructions below are for using Logger Pro® software.

Logger Pro is available from www.oit.duke.edu for free download. There are both PC and Macintosh versions available. There are complete download and installation instructions in the Documents section of the Sakai site for the course. See your TA or the Lab Manager if you have any problems or questions. After installing we suggest you update to the latest version at www.vernier.com.

Data visualization using Logger Pro

1. Click on the 

icon on the Windows or Macintosh Desktop to start Logger Pro. The program will load and you will see the main screen.

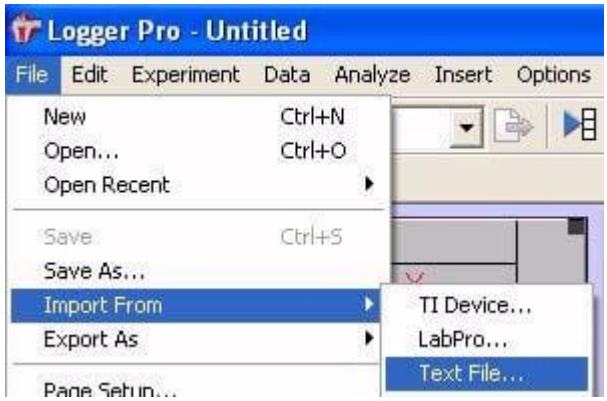


Figure 11.4.1: Import function on Logger Pro.

2. Select Import From and Text File from the File menu. Locate and Highlight your first runa1X.txt file in the Open dialog box. Click Open to import the data file into Logger Pro.

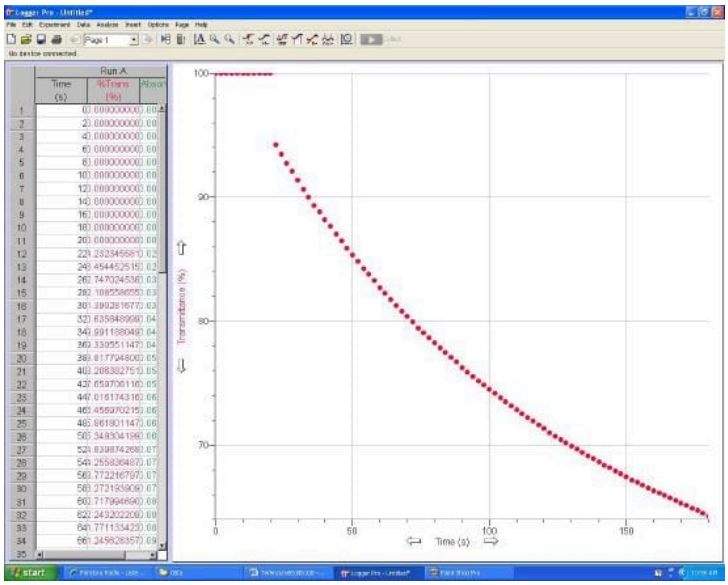


Figure 11.4.2: Copy and Paste Caption here. (Copyright; author via source)

The data file will be entered into the table on the left of the screen and a graph of transmittance vs time (in seconds) will be displayed in the graph window. Double-click the word Latest appearing at the very top of the Data Table. A Data Set Options box appears. Change the name of the data set to Run A.

3. Repeat Step 2 three more times opening the second, third and fourth data files from your experimental work. With each new file opened data columns will be added to the table and graph window. Change the Data Set names to Run B, Run C and Run D respectively.

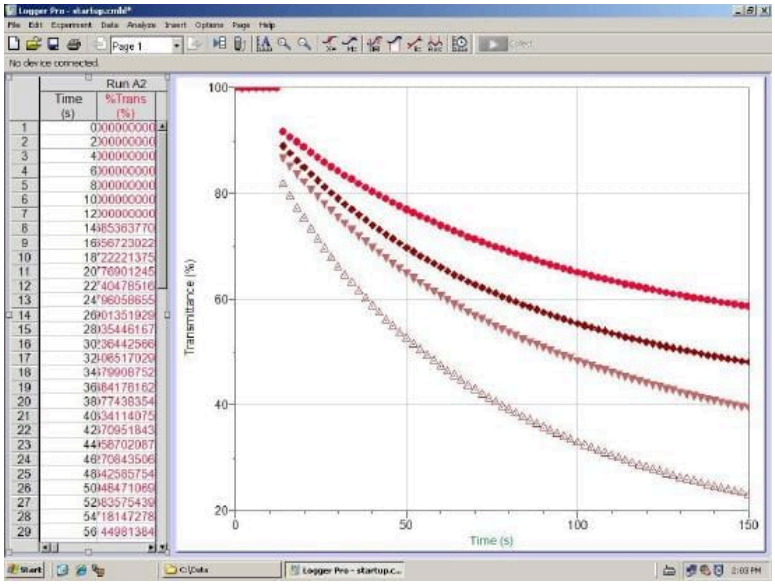


Figure 11.4.3: Transmittance vs time plot.

4. Select Graph Options from the Options menu. Make sure Connect Points is NOT checked in the Graph Options tab of the Graph Options dialog box. Check Point Symbols. Click on the Axis Options tab. Un-check Transmittance and put a check in Absorbance in each one of the four data sets. (Run A though Run D). You will have to click the little + to the left of the column titles to see the Absorbance check boxes. Check to be sure the Scaling is set to Autoscale for both X- and Y-axes. Click Done. Your graph window will update to show the absorbance vs. time data for your first assay.

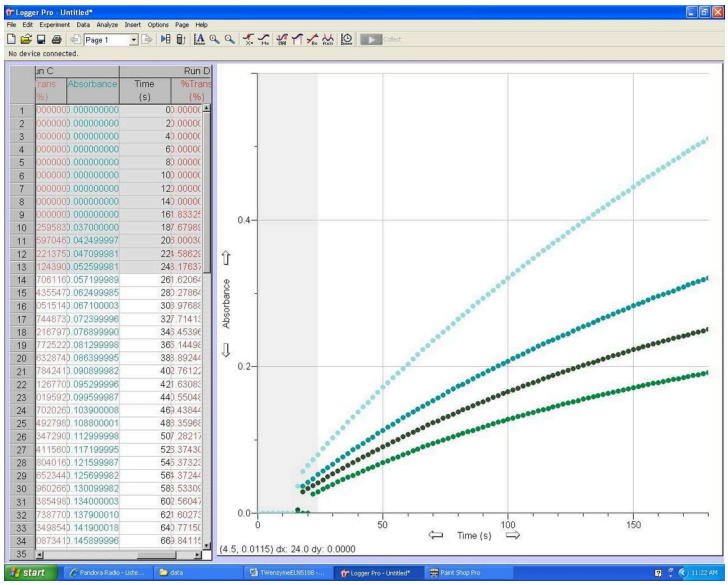


Figure 11.4.3: Absorbance vs time plot.

5. Move now to the table window. Slide the horizontal scroll bar at the bottom of the data table window all the way to the left. Notice that for the first approximately 20 seconds of each run the absorbance is zero – because you were adding the enzyme, mixing the reaction and putting the cell into the spectrometer during this time. Click and drag the mouse, down and to the right, to highlight all of the data cells that represent zero absorbance, and maybe a few cells with non-zero absorbance. These data are suspect because you were setting-up the reaction and spectrometer.

   Hit the Delete key on the keyboard to remove these data from the runs. This will leave only the stable and reliable data from the four runs. You should now see a nice view of how the absorbance varies with time for each of the four runs (i.e., for the four different substrate concentrations).

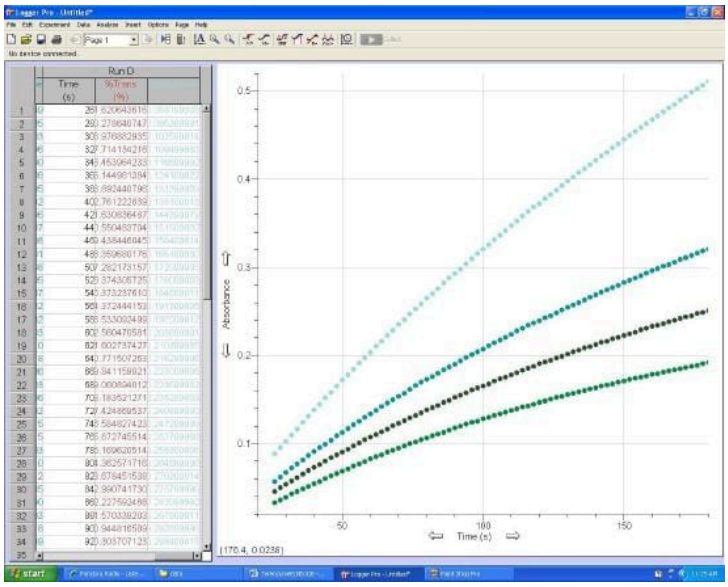
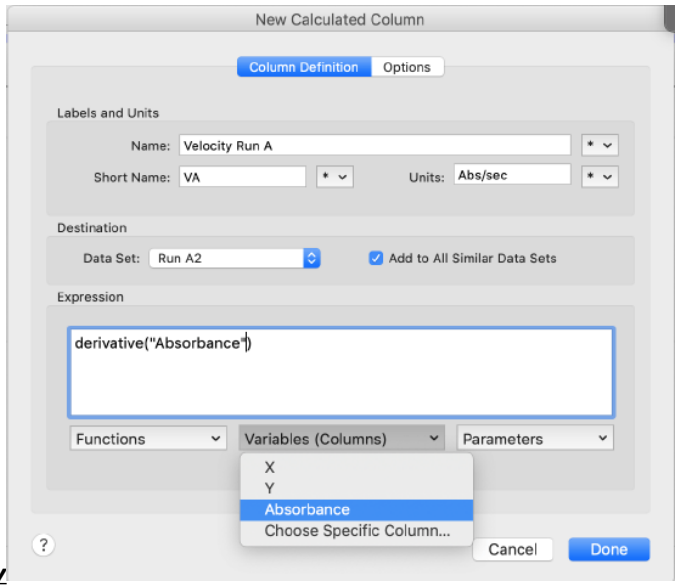


Figure 11.4.4: Absorbance vs time with initial points removed

6. Select Save from the File menu to save your work.

Data Analysis using Logger Pro

The kinetic data are analyzed using Logger Pro® software. The first step is to calculate reaction velocity from the absorbance vs. time data for each of your runs.

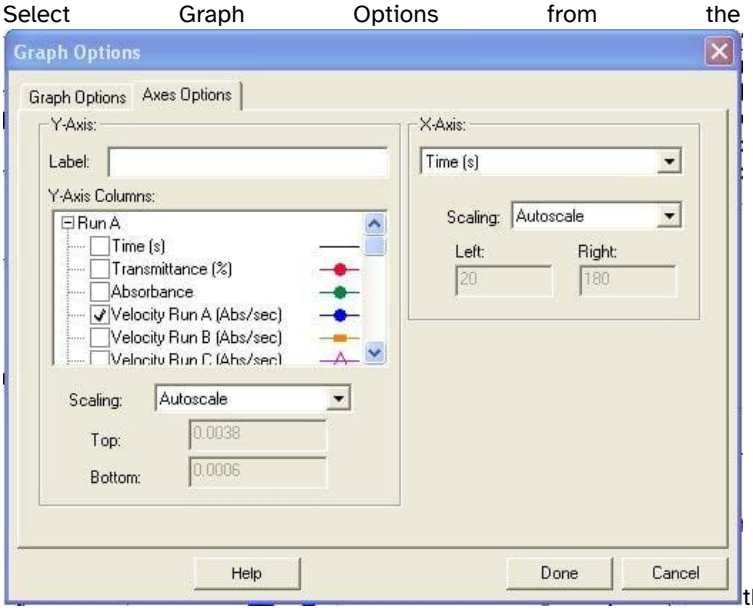


A. Steps 1-9 must be completed before leaving the laboratory

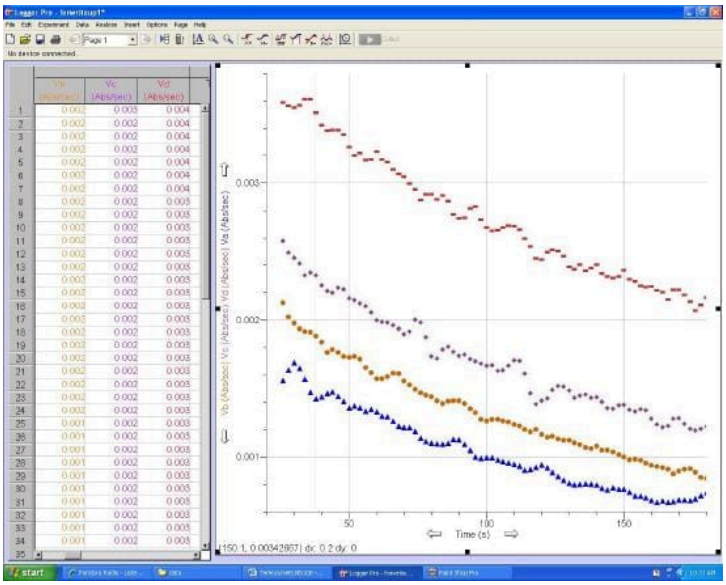
1. Select New Calculated Column from the Data menu. A New Calculated Column dialog box opens. Enter a name and a short name for this new column. Enter the units (Abs/sec). Also select the Data Set from the drop-down menu. Leave check Add to All Similar Data Sets.
2. Click on the Functions > button in the New Calculated Column dialog box. Select Derivative from the Calculus option. Go to the pull-down menu under Variables (Columns) and Select Absorbance. Then click Done in the New Calculated Column box.



3. Select Graph Options from the Options menu. Select

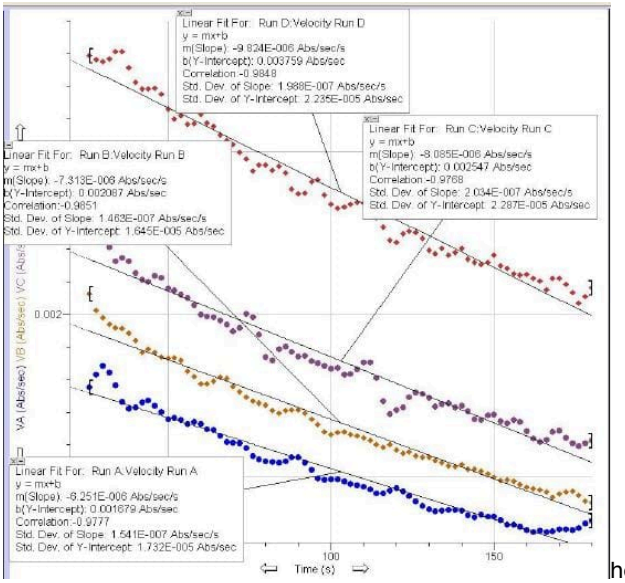


the Axis Options tab. Remove the checks from Absorbance in each of the four runs and put checks in the appropriate Velocity columns so as to show velocity vs. time for runs A through D.



4. Click Done to close the Graph Options box. Your velocity data should look something like this image shown here.

5. To do a Linear Least-Squares analysis of these velocity lines, click the  button found in the button bar at t



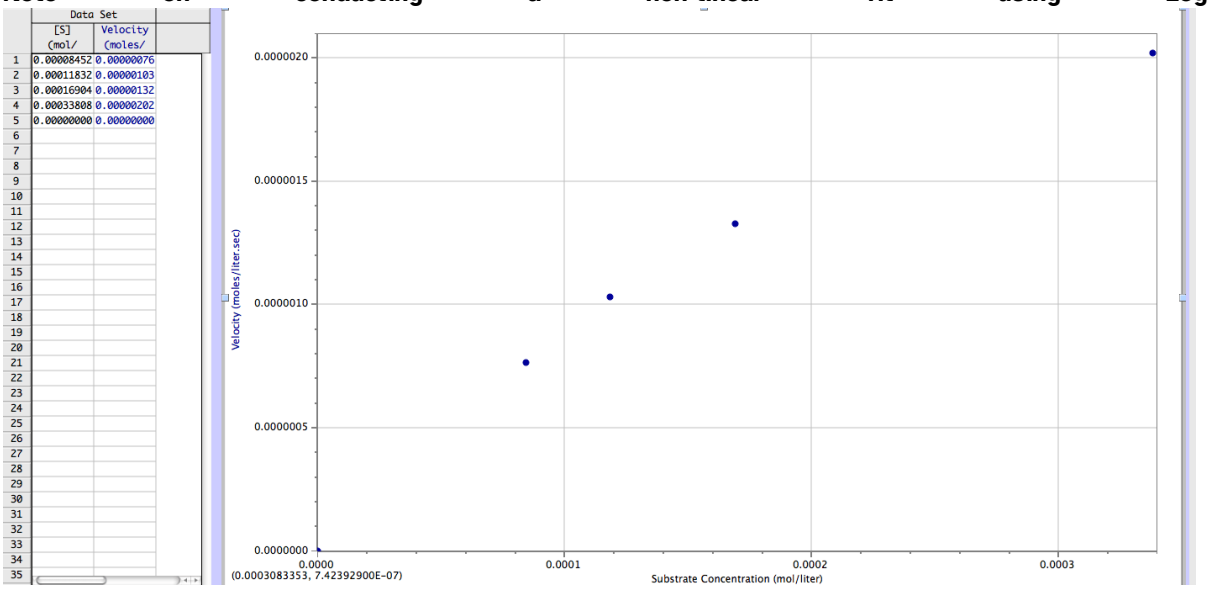
he top of the Logger Pro screen. A Select Columns dialog box will appear. The four velocity columns should already be highlighted within this box; if not, highlight all four. Click OK to close the Select Columns box. You will see Linear Least-Squares lines appear in the graph window. There will also be an information box associated with each Linear Least-squares line where you will see values for the slope, intercept and correlation.

6. Double-click inside one of these information boxes. A Linear Fit Options box appears. Check Show Uncertainty, and click OK. The standard deviation of the slope and intercept will be added to the information box. You can use these as a good estimate of the uncertainty in slope and intercept of your linear fit. Repeat this procedure for the other three linear fit lines.
7. Repeat the procedure with your second set of runs. Review the data with your TA to be sure you have sufficient results to continue with the analysis. The intercepts are estimates of the initial velocities of the reactions. You should see good agreement in these values for the replicate runs for each substrate concentration. If not, you should do another run of that substrate concentration.
8. Save all of your data files (.txt files) and this Logger Pro file in a single folder and upload it to Sakai so that you have access to it outside of lab.

b. Outside Lab: Complete the Following Calculations and Questions

1. Create a table or an Excel spreadsheet that summarizes the results. For each concentration of L-DOPA, calculate the mean initial velocity from your replicate runs, and use this value of V for further analysis.
2. Using the Beer-Lambert law (equation 19), and the molar absorptivity of dopachrome at the peak maximum of the band in the visible spectrum (3500 M–1 cm–1), convert each value of V into units of moles liter–1 sec–1.
3. Analyze the dependence of velocity (V) on L-DOPA concentration (in units of moles per liter) using (1) a non-linear, curve fit to the Michaelis Menton Equation (see below); and, a Lineweaver-Burk plot and (2) either the Eadie-Hofstee plot (for students with family names beginning A-M) or the Hanes-Wolf plot (for students with family names beginning N-Z) plot. Evaluate KM and Vmax. Discuss the relative merits of each treatment.
4. Approximate k2 using Eq. (10). Show a sample calculation.

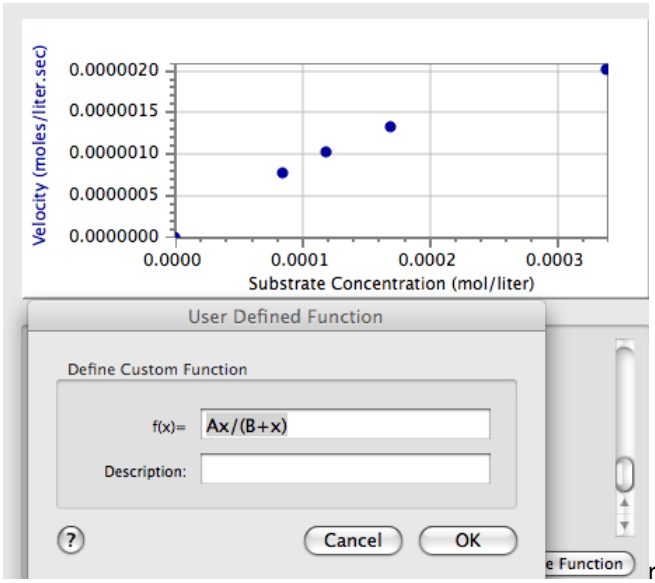
Note on conducting a non-linear fit using Logger Pro:



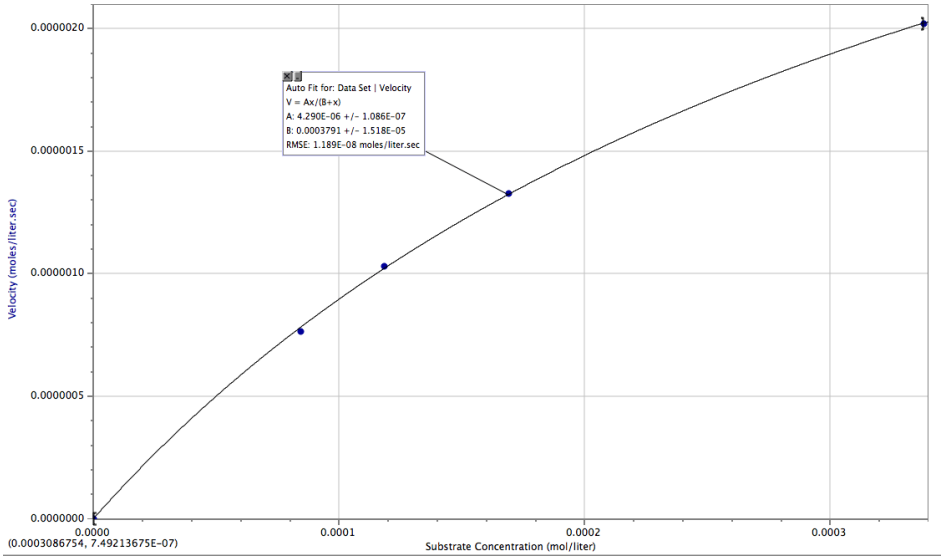
1. Open Logger Pro and enter your initial velocity vs. substrate concentration data. You might want to add a point representing zero velocity at zero substrate concentration. A graph of your data will appear in the Graph Window (be sure you are not connecting your data points with a line).

2. Select Curve Fit from the Analyze menu. Click on the Define Function button in the Curve Fit window. Enter the form of the Michaelis-Menton Equation as Ax/(B+x) where, A = Vmax; x = substrate concentration; and, B = Km. Click OK.

3. Click on the Try Fit button. A curve fit will be created and results for the variables A and B (i.e., Vmax and Km) will be displayed in the right hand side of the window.



4. Click OK, and you will be returned to the main Logger Pro Window. You will see the curve fit through the data and you will also see a data box giving the equation for the curve and the values for the variables. Double click on this box and set it to show 4 significant figures. Also turn on Show Uncertainties and Display on Graph.



Discussion Questions:

This section should include (but not be limited to) the following:

1. A qualitative description of uncertainties, noting the most significant uncertainties and the extent to which they affect the results. *(In other words, consider all the measurements that have gone into this work (including measurements involved in creating stock solutions, reaction solutions, and absorbance readings. How do these measurements contribute to the accuracy of your results, and which are most significant?)*

2. A discussion of the importance of controlling reaction conditions (*consider concentration, pH, temperature, timing*).

3. An interpretation of the kinetic results with the assumption that k_2 refers to the decomposition of the enzyme-substrate complex (equation (2)) and that K_M is related to the affinity of the enzyme for the substrate (equation (11)). Literature values are available and you should find at least two or more sources.

4. Discuss the dependence of V on the concentration of substrate.

5. Discuss the relative merits of the non-linear (the Lineweaver-Burk treatment) and the linear (Eadie-Hofstee or alternative Hanes-Wolf) treatments of your data.

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11.5: Discussion

This section should include (but not be limited to) the following:

1. A qualitative description of uncertainties, noting the most significant uncertainties and the extent to which they affect the results.

2. A discussion of the importance of controlling reaction conditions.

3. An interpretation of the kinetic results with the assumption that k2 refers to the decomposition of the enzyme-substrate complex (equation (2)) and that KM is related to the affinity of the enzyme for the substrate (equation (11)). Literature values are available and you should find at least two or more sources.

4. Discuss the dependence of V on the concentration of substrate.

5. Discuss the relative merits of the non-linear fit; the Lineweaver-Burk treatment; and, your other linear treatment (Eadie-Hofstee or alternative Hanes-Wolf) of your data.

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11.6: References

NOTE: All books referenced below (with the exception of journal articles) should be found on closed reserve at the Perkins Circulation Desk. Please ask for them there. Please ask the librarian for assistance.

1. Graham, D. G., Jeffs, P. W., J. Biol. Chem., 1977, 252, 5729.

2. Swan, G.A., J. Chem. Soc. Perkin Trans. I, 1976, 339.

Additional Reading:

a. Bettelheim, F. A. Experimental Physical Chemistry, W. B. Saunders Co., Philadelphia, PA 1971, pp. 297-304.

b. Dawson, C.R.; Tarpley, W.B. in The Enzymes, Vol. II, Part 1, Summer, J.B.; Myrbäck, K. (Eds.), Academic Press, NY, 1951, Chapter 57. (Call #:612.015S956E).

c. Alberty, R.A. and Silbey, R.J. Physical Chemistry, 2nd Ed., John Wiley and Sons, New York, N.Y., 1992, Chapter 20, Section 20.11.

d. Atkins, P.W. Physical Chemistry, 6th edition, W.H. Freeman and Co., NY, 1997, Chapter 25, pages 780-784.

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12: ARCHIVE

12.1: References and Additional Reading
12.2: Instructions for using the UV-Vis Spectrophotometers
12.3: TA Notes
12.4: Introduction to Huckel MO Theory
12.5: Hückel Calculations Using Hulis (Part II)
12.6: Introduction to Particle in a Box applied conjugated molecules
12.7: Proceedure and Treatment of Data (Part I)

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12.1: References and Additional Reading

Duke students can find additional reading materials at the link below, many of which are listed in the references below.

Duke students, click here for additional readings, or find the resources below in the Library (yes, the physical library!)

References

1. Castellan, G. W., Physical Chemistry, Addison-Wesley, Reading, Mass., 1972, Chapters 19-22.

2. Barrow, G. Physical Chemistry, 3rd ed., McGraw-Hill, New York, NY, 1973, Chapters 3 and 12.

3. Shoemaker, D. P., Garland, C. W., and Nibler, J. W. Experiments in Physical Chemistry, 6th ed., McGraw-Hill, NY, 1996, Chapter XIV, Experiment 34.

4. Farrell, T.T., J. Chem. Ed., **1985**, 62, 351.

5. Olsson, L.F., J. Chem. Ed., **1986**, 63, 756.

6. Kuhn, H., J. Chem. Phys., **1949**, 17, 1198.

7. Herzfeld, K.F.; Sklar, A. L. Rev. Mod. Phys., **1942**, 14, 294.

8. Silbey, R. J., Alberty, R.A., and Bawendi, M.G., Physical Chemistry, 4th ed., Wiley, NY, 2005, Chapter 9, Section 9.6; Chapter 11, Section 11.7.

9. Cotton, F.A., "Chemical Applications of Group Theory", Wiley, New York, 1971, Section 7.1 and pp. 366-367.

10. Suzuki, H., "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, 1967, Chapter 17, p. 374.

11. Aldrich Catalog, Aldrich Chemical Company, Inc., 1992., found in FFSC 1113 or online.

12. Venkataraman, K., "The Chemistry of Synthetic Dyes", Academic Press, Inc., NY, 1952, Volume II, Chapter XXXVIII, p. 1155.

13. Streitwieser, A., "Molecular Orbital Theory for Organic Chemists", John Wiley & Sons, Inc., NY, 1967, Chapter 2.

14. Okawara, M., Kitao, T., Hirashima, T., and Matsuoka, M., Physical Sciences Data 35: Organic Colorants, Kodansha, Tokyo; Elsevier, Amsterdam-Oxford- New York-Tokyo, 1988, pp. 318-321.

15. Taubmann, G., J. Chem. Ed., **1992**, 69, 96.

16. Atkins, P.W. Physical Chemistry, 5th ed., W. H. Freeman, NY, 1994, Sections 12.1, 14.9, or, 6th ed., W. H. Freeman, NY, 1997, Sections 12.1, 14.9.

17. Engel, T., Drobney, G and Reid, P., Physical Chemistry for the Life Sciences, Pearson Prentice Hall, NJ, 2008 (Section 14.3).

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12.2: Instructions for using the UV-Vis Spectrophotometers

Below are the instructions for using the Agilent Cary Series UV-Visible spectrophotometer in the Absorption Spectrum of Conjugated Dyes experiment.

There are two sample holders in the instrument. The Sample is placed in the front holder. A Reference cuvette can be placed in the back holder or the back holder can be left empty (no cuvette).

Start-up:

At the begriming of the lab period, check to confirm that the UV-vis is switched "on". There are several UV-vis instruments in the Duke Chemistry undergraduate learning spaces. Be sure you discuss which instrument you will use with your instructor.

- The **Cary 100** instruments have tungsten and deuterium lamps that must be warmed up for approximately 1 hour prior to use for best results. However, since we are only doing qualitative analysis, it is sufficient for this experiment to warm them up for only a couple of minutes.
- The **Cary 60** instrument has a xenon flash lamp, which does not require warm up.

How to turn on the Cary 100: With both sample and reference holders empty and the cover closed, turn on the instrument with the switch at the front, lower left. Wait two minutes before proceeding further.

How to turn on the Cary 60: The Cary 60 should not be turned off. But, if it is off, check that the cell holders are empty and press the power button on the instrument.

Validating the Wavelength Accuracy of the UV-Vis Spectrometer

1. Open the Validation Software by clicking the  icon from the Windows main screen. After a few moments the software screen will appear and will begin to communicate with the instrument. You can follow the progress by monitoring the display at the lower left of the screen. When the traffic light in the upper center turns green, the system is ready. You will see absorbance in the upper left and wavelength in the upper right.

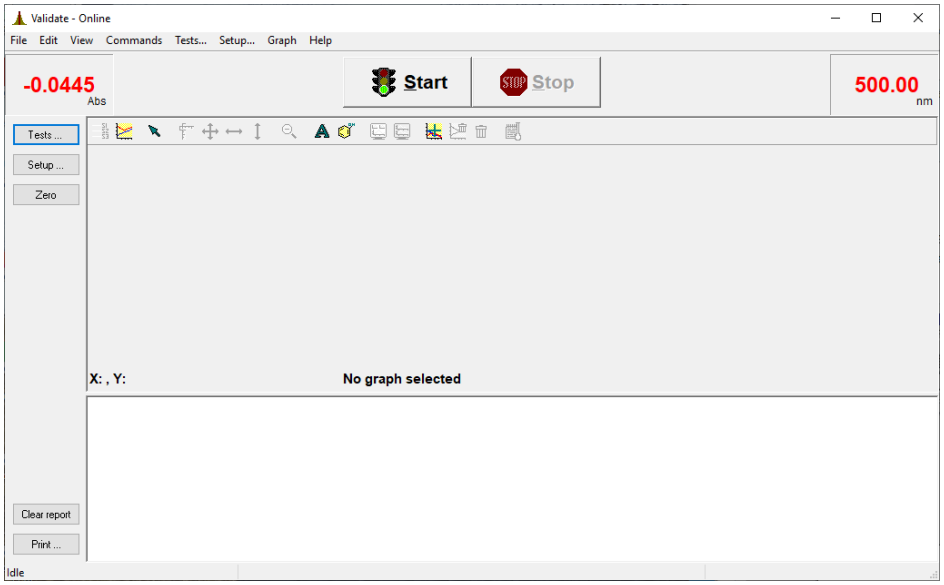


Figure 12.2.1: The Validate Main Screen. (CC-NC-BY-DUKE CHEM)

2. Click the 

button and select Instrument Performance Tests. While you could run all of the tests listed, the one that is required is the Wavelength Accuracy test. Depending on whether you are using a Cary 100 or a Cary 60, this test with use either the D2 or Xe lamp. Be sure to note which instrument you are using and which lamp is used for the wavelenght validation.

   Using the  button, you can remove all tests from the list except for the Wavelength Accuracy. The screen should look as shown here.

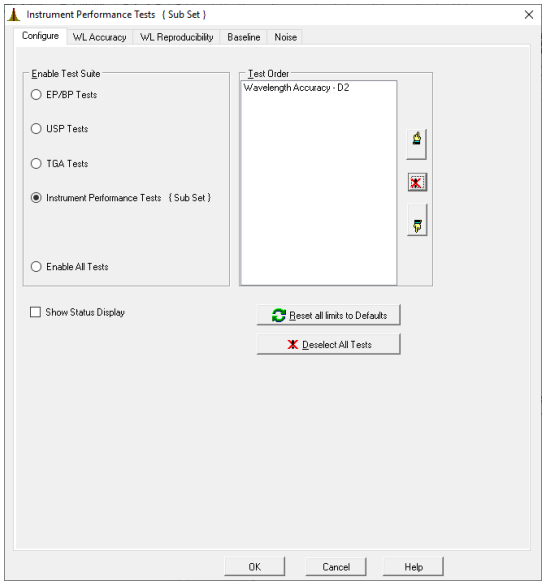


Figure 12.2.2: Selecting the Wavelength accuracy test. (CC-NC-BY-DUKE CHEM)

3. Click the 

button and, when the setup screen appears, place your names in the Name line; and, the name of the test in the comments box. In the Options section select Auto Print, Results and Graph. Data Form and Company Logo should not be checked. % Page Height set at 50 is fine.
4. Click 

to return to the main screen.
5. Check the sample compartment to be sure that there are no samples in the instrument and that there is nothing blacking the light path. Gently close the sample compartment.
6. Click 

to begin wavelength accuracy test. As the test proceeds the emission spectrum from the lamp will be displayed. At the conclusion of the test, a report will be generated on the screen. **Include these data in your laboratory report**. Check to be sure that the difference between the expected and observed peak positions is one the order of $\pm 0.2 - 0.4$ nm. If it is greater than that, consult your TA or your Instructor before proceeding further.

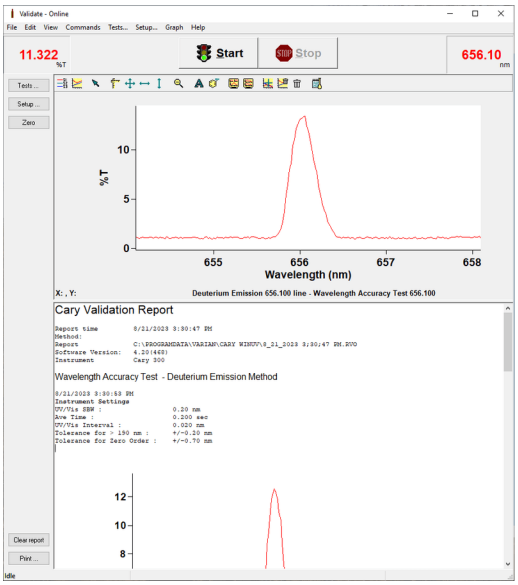


Figure 12.2.3: Results of the a Wavelength Accuracy Test using the Deuterium lamp emission on a Cary 100 series spectrophotometer. (CC-NC-BY-DUKE CHEM)

7. Exit the Validation software and return to the Windows Desktop.

Absorption Spectrum of Conjugated Dyes

1. Load the Scan Software by clicking the  icon on the Windows main screen. In a few moments the scan software main screen will appear and will begin to communicate with the instrument. You can follow the progress by monitoring the display at the lower left of the screen. When the traffic light at the top center of the screen turns green, the system is ready. You will see absorbance at the upper left and wavelength at the upper right of the screen.

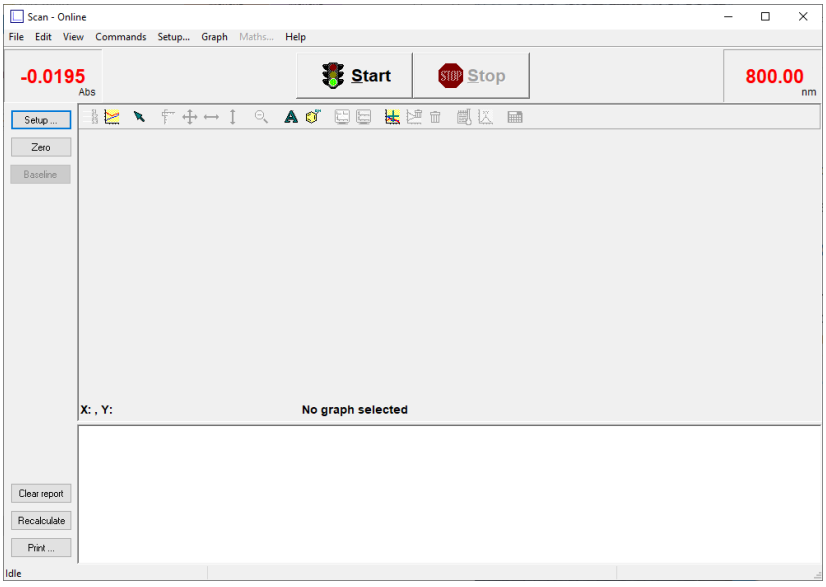


Figure 12.2.4: The Scan Module Main Screen. (CC-NC-BY-DUKE CHEM)

2. Click the  button and wait for the setup screen to appear. Select, first, the Cary tab to begin setting parameters for your sample runs. Under X-mode, the Mode should be set to nanometers and your scan range from 750 nm to 400 nm. Under Y-mode, the Mode should be set to absorbance and the range from (-)0.05 to 1.0. The Ave time should be

0.1 seconds and the Data interval should be set to 1 nm. This will yield a Scan Rate of 600 nm/min.

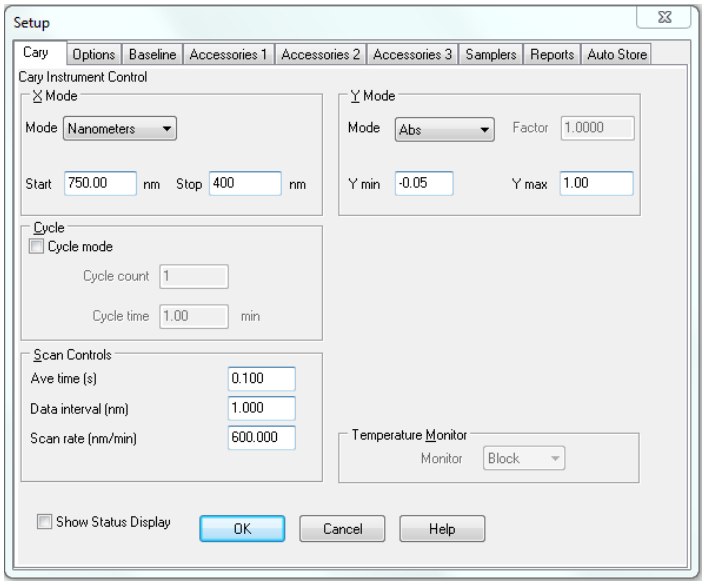


Figure 12.2.5: The Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

3. Select the Options tab on the setup screen and set the Spectral Band Width (SBW) to 2 nm. Select Double Beam Mode. Select UV-Vis as the source and be sure the Source changeover is set to 350 nm. Under Display options you can choose Overlay Data.

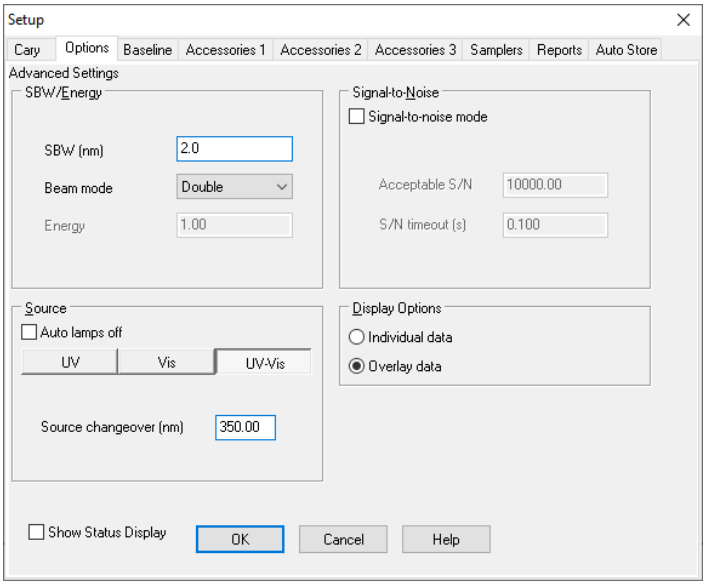


Figure 12.2.6: The Options Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

4. Finally, select the Reports tab.
   - Put your names in the Name box and the title of the experiment in the Comment box.
   - In the Options box, check Data Form, Graph and Focused trace. Do not check Auto print, or Parameters. Select All Traces. And % Page Height set at 50 is fine.
   - Under Peak Table, put a check in All peaks.
   - Be sure the Include XY pairs table is not checked.
   - Click the Peak Information button, and set the Threshold to 0.200. Put Peaks in the Peak Type box.
   - Click OK to close the Peak information box, and OK again to return to the main screen.

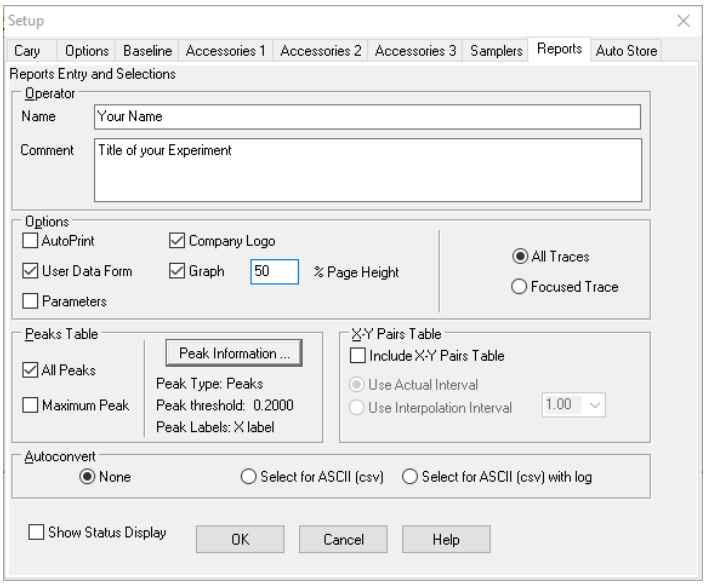


Figure 12.2.7: The Reports Tab of the Scan Setup Screen. (CC-NC-BY-DUKE CHEM)

5. Place your first sample in the sample compartment and if you are using a reference cuvette, put your reference in the reference compartment and close the cover.
6. Click 

to begin the run.
7. You will be prompted for a filename. Since you will be running four samples, give the file a general name, for example Dyes with the date (many sample spectra can be stored in a single file).
8. You will then be prompted for a sample name. Place the name of the sample (Dye 1, 2, 3, or 4) in this box.
9. As each run proceeds you will see the spectrum generated in real time on the screen. Make sure the maximum absorbance of each sample is between approximately 0.2 and 1.0; adjust the dye concentration to get the proper absorbance.
10. At the conclusion of each run, place the next sample in the sample compartment and initiate the new scan.

Note

If you didn't select Overlay Data, or if you want to add or remove traces from the overlaid runs on the screen, click the  button at the upper left of the main screen. Select files to add or to remove by checking or removing cheks from available traces shown in the list. Then click OK. Your changes will be made to the main screen.

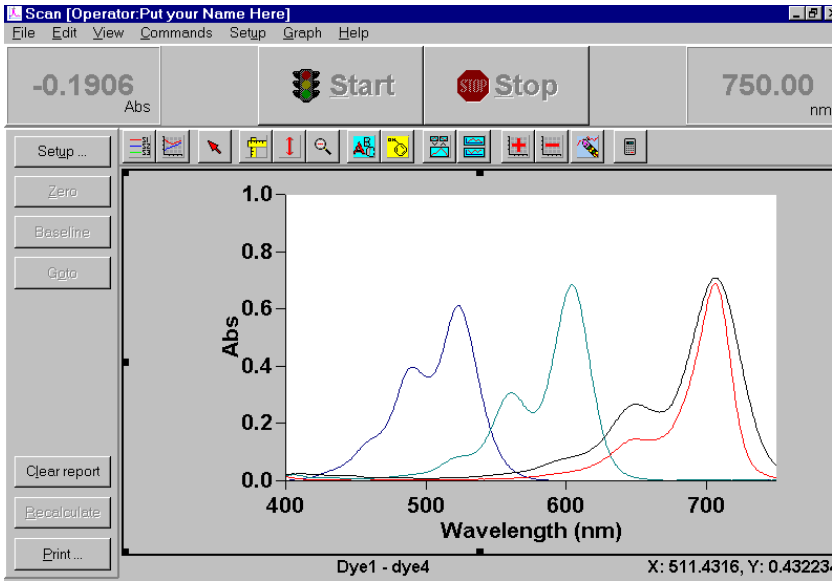


Figure 12.2.8: The Absorption Spectra of the Dyes. (CC-NC-BY-DUKE CHEM)

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12.3: TA Notes

This page is directed toward laboratory teaching assistants, but is deliberately left open for students to read.

TA Notes

After completion of this module students will be able to:

- Use online resources to find expected values for λ_{max} for the dyes
- Follow instructions to operate a UV-visible spectrophotometer
- Apply chemical theories (particle in a box) to explain experimental observations
- Use programing skills and computational software (MatLab) to analyze data
- Practice recording observations in an electronic laboratory notebook (ELN)
- Apply knowledge of chemical theories and data to describe and discuss results

Pre-Semester Preparations

Do the following during the TA training week(s)

1. Check that the materials listed below are available and sufficient for all students to use them. All items are in the prep room on the shelves and in the refrigerator/freezer.
   If they are running low, please create more or inform the instructor. Each group of 3-4 students will need the following:

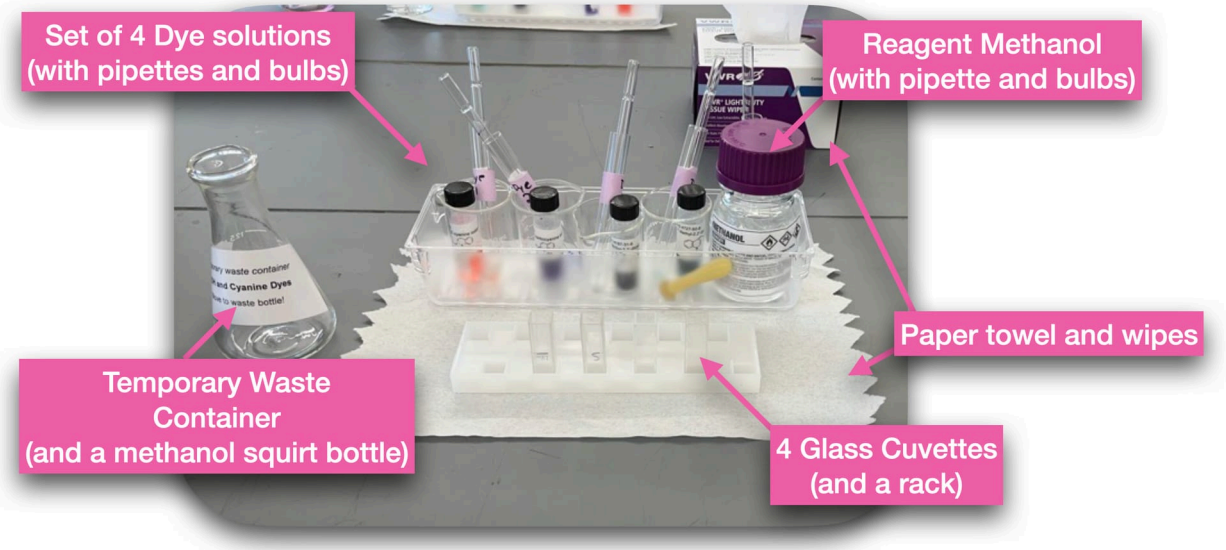


Figure 12.3.1: The materials needed to complete this experiment are shown in this picture. (Kathryn Haas; CC-BY-NC-SA)

   - **Set of 4 Dye solutions**: One set of the dye solutions
   - **Methanol reagent**: One small bottle of reagent methanol for diluting the dye solutions.
   - **At least five glass Pasteur pipettes:** one for "clean" methanol, and one for each dye solution.
   - **Bulbs**: at least three bulbs to be used by multiple students preparing solutions.
   - **Set of 4 glass cuvettes:** One cuvette for each dye solution
   - **Cuvette rack:** One is required, two racks is ideal.

**Teach students to always keep cuvettes in a rack or instrument cell holder, never directly on the bench.

- **Methanol wash bottles**: Be sure that there is one full methanol wash bottle available for each group. This is for rinsing cuvettes.
- **Lab wipes** (ie Kimwipes) for wiping cuvettes.
- **Paper towel mat** to catch spills. Additional paper towels are at sink areas.

2. Complete instrument training with Dr. Haas.
3. Perform the entire experiment as if you were a student.
4. Write and submit a report as if you were a student.
5. Practice grading your and your partner's report using the grading rubric.

Pre-Lab Preparations

When you are on TA duty, arrive at least 20-30 minutes early to prepare and ready the materials listed above for students. Most of the set-up can be done ahead of time, but dye solutions should be kept cold when not in use.

- Take dye solutions out of freezer and place them at student stations.
- Check that dye solution colors are as expected (see Figure 12.3.2).
  - **Dye #1**: 1,1'-diethyl-2,2'-cyanine iodide is **pinkish-orange.**
  - **Dye #2**: 1,1'-diethyl-2,2'-carbocyanine chloride is bright **blue** (not purple at all!)
  - **Dye #3**: 1,1'-diethyl-2,2'-dicarbocyanine iodide is dark **turquoise**.
  - **Dye #4**: 1,1'-diethyl-4-4'-carbocyanine iodide is **dark blue** (not yellow/green/brown color)
- At the UV-vis instrument and computer:
  - Turn on the UV-vis if you'd like to allow it to warm up.
  - Create a file folder for that day's section in the course directory on the computer hard drive.
  - Put the most recent version of the ELN on the UV-vis computer you will use.



Figure 12.3.2: Check that the dye solutions are not degraded by comparing their colors to this figure or to the dye stocks that are always stored in the freezer. (Kathryn Haas; CC-BY-NC-SA)

Helping your students

During the laboratory session, you are expected to be present and available for the entire 4.5 hours. Your job is to help students to complete the experiment safely and successfully, while upholding expectations and academic standards for the students.

In this particular laboratory session, please provide guidance and instruction on the following:

- **Creating the solutions for analysis**: Students will put a few drops of the concentrated dye solutions into the cuvette and

dilute with methanol. Please have an idea of what the solutions should "look like" (ie how dark/concentrated the should they be so that students can collect usable spectra). And, please make sure students are filling their cuvette about 3/4 full (not too full that it spills in the spectrometer, but full enough so that the light beam goes through the solution).
- **Using the spectrometer**: Be ready to step in if the students ask for help while validating the instrument and taking the spectrum. Be able to answer questions like "do I need to put a blank cuvette in the back"? "Do I need to take a baseline"? "Why does my spectrum look all noisy at Abs = 3? "Why do we need glass cuvettes - can I use quartz?"
- **Annotating spectra:** Show students how to add their wavelengths and label the Dyes on the spectrum through the annotation tool.
- **Saving data:** Please direct students to the folder in the course directory and instruct them to save their data to that folder using the format "YYYMMDD_filename_comments"
- **Filling out their ELN:** Be aware of what information the students should put in their ELN and guide them appropraitely. If they are moving on to the next step without recording the data, please remind them to do so. But, please let students do it themselves.
- **Taking turns:** Please help students to take turns controlling the instrument. Each student should be allowed to collect and annotate at least one spectrum.
- **Using the custom "dye" script in MatLab:** Be familiar with the script and how it is used, and guide students through the steps as necessary.

Encourage students to proceed through the data analysis and complete the ELN prior to leaving the lab. Remember, your role is as their coach - help encourage them to get their work done now while help is available so they do not feel overwhelmed later. If they need to take a bathroom or snack break, encourage them to do so before returning to the classroom room to complete the exercise.

Shut down/ clean up

Unless there is an unforeseen issue, your students should be finished with the lab work before 5 pm. They are to leave the room in clean condition prior to leaving lab and returning to the conference room.

- Remind students to clean up before returning to the classroom. Students should do the following:
  - Clean cuvettes with rinse methanol three times and leave the cleaned cuvettes in the rack.
  - Empty the temporary waste container into the primary waste container labeled for this experiment. Rinse the flask into the primary waste using rinse methanol.
  - Return the temporary waste container to the bench
- TAs should do the following shut down tasks before returning to the classroom:
  - Encourage students to continue their work in the classroom until their ELN is complete.
  - Turn off the UV-vis.
  - Return the dye solutions to the freezer.
  - If you are the last section of experiment, return all materials to their storage location in the prep room.
  - Be sure that the primary waste container is capped.
  - Remind students to clean up.
- Remind students to sign out with the time they leave and get your signature.
- Check the TA checklist for additional items to be completed.

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12.4: Introduction to Huckel MO Theory

Definition: Conjugation

A conjugated π system is one that contains alternating single and double or triple bonds along a chain of carbon atoms. The most common type of conjugation is alternating double and single bonds. A simple example is the butadiene molecule. $H_2C{=}CH{-}CH{=}CH_2$

The Particle-In-A-Box approximation

Electrons in the π-electron system of a conjugated aromatic compound are not restricted to specific nuclei but are free to move throughout the system. In a linear conjugated system the potential energy of the electrons will vary along the chain, being lowest near the nuclei and highest between them. To a first approximation, however, it can be assumed that the potential energy of the electrons is constant along the length of the chain and increases to infinity one bond distance beyond the end atoms of the chain. The electrons may be visualized as being contained in a one-dimensional potential well, of length ℓ, and occupying orbitals of different energy within the well. The wave functions representing the orbitals and the energy levels of the orbitals can be obtained by solving the Schrödinger equation for this system.

For a one-dimensional system the Schrödinger equation takes the form

$$\frac{\partial^2 \psi_{(x)}}{\partial x^2} + \frac{8\pi^2 m}{h^2}\left(E - V\right)\psi_{(x)} = 0 \tag{12.4.1}$$

where $\psi_{(x)}$ are wavefunctions that satisfy the equation (eigenfunctions), E is the energy of the particle of mass m, V is the potential energy, and h is Planck's constant.

The potential energy, V, is a constant within the well of length ℓ, where $\psi_{(x)}$ must vanish for $x \leq 0$ and $x \geq \ell$ and $V = \infty$. This allows us to conveniently set V equal to zero in the region $0 \leq x \geq \ell$ when deriving solutions of the equation. The equation then reduces to

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2 \psi_{(x)}}{\partial x^2} = E\psi_{(x)} \tag{12.4.2}$$

Solutions of this equation are $\psi_{(x)} = A \cdot \sin\left(\frac{n\pi x}{\ell}\right)$, where A is a constant and n = 1,2,3,... etc.

Verification that this wave function is indeed a solution of the Schrödinger equation may be obtained by substitution into the left- and right-hand sides of the above equation.

$$\begin{aligned}\text{Left-hand side} &= \frac{-h^2}{8\pi^2 m}\left(\frac{-n^2\pi^2}{\ell^2}\right) A \cdot \sin\left(\frac{n\pi x}{\ell}\right) \\ &= \frac{-h^2}{8m\ell^2} A \cdot \sin\left(\frac{n\pi x}{\ell}\right) \\ \text{Right-hand side} &= EA \cdot \sin\left(\frac{n\pi x}{\ell}\right)\end{aligned}$$

The function $\psi_{(x)}$ is a solution of the Schrödinger equation when the energy E of the system has the values $E = \frac{n^2 h^2}{8m\ell^2}$. The allowed energy levels are depicted diagrammatically below.

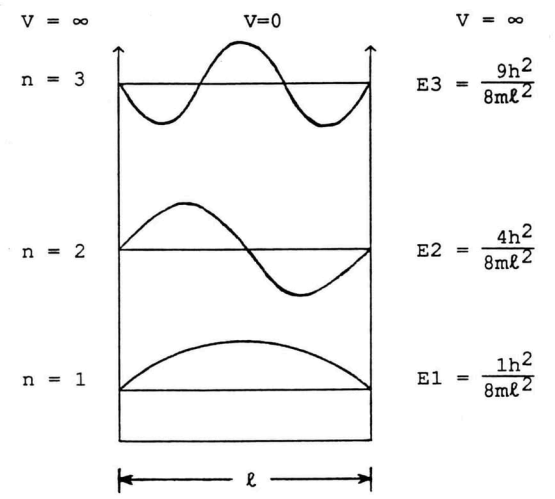


Figure 12.4.1: The Particle-in-a-Box Model.

The ground state configuration for the conjugated system of a molecule is derived by allocating two electrons to each of the energy levels in accord with the Pauli exclusion principle. Thus, a molecule with Nπ electrons will have the N/2 lowest levels filled and all the higher levels empty. When the molecule absorbs UV-vis light, the energy absorbed is from an electron in the HOMO (where n = N/2) becoming excited to the LUMO where n = (N/2) + 1. The energy change, ΔE, for this transition is

$$\begin{aligned}\Delta E &= E_{\left(\frac{N}{2}+1\right)} - E_{\left(\frac{N}{2}\right)} \\ &= \frac{\left[\left(\frac{N}{2}\right)+1\right]^2 h^2}{8m\ell^2} - \frac{\left(\frac{N}{2}\right)^2 h^2}{8m\ell^2} \\ &= \frac{(N+1)\,h^2}{8m\ell^2}\end{aligned}$$

Since $\Delta E = h\nu = \frac{hc}{\lambda}$ where c is the speed of light and λ is the wavelength, then

$$\lambda = \frac{8mc}{h}\frac{\ell^2}{(N+1)} \tag{12.4.3}$$

Thus if ℓ is known, this relation can be used to calculate the wavelength maximum of the band representing the transition from the ground state to the first excited state in a π-electron system.

PIB model for cyanine dyes:

This Particle-in-th-Box model can be applied to carbocyanine dyes which may be represented, for example, by the resonance forms shown below for the 1,1'- diethyl-4,4'-carbocyanine (cryptocyanine) cation.

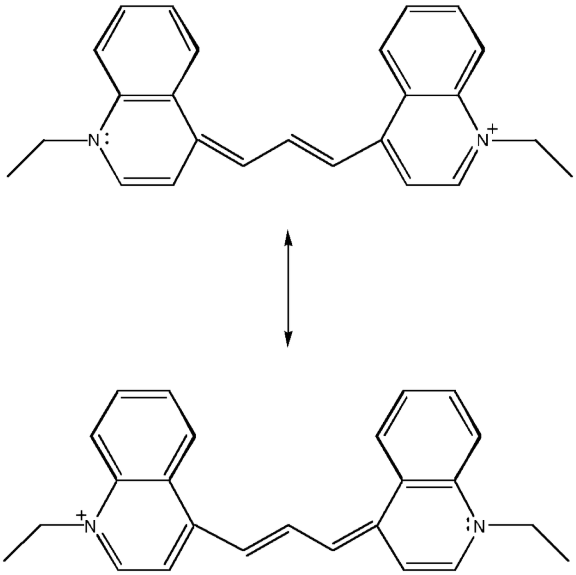


Figure 12.4.2: The *1,1'-Diethyl-4,4'-carbocyanine (cryptocyanine) cation*. (CC-NC-BY-DUKE CHEM)

The π-electrons in the molecule are regarded as a collection of "free" electrons (independent particles) confined to a box, whose wavefunctions are the square-well functions. Once again, these electrons are distributed among the wavefunctions and energy levels according to Pauli principles, so that the absorption of energy (light) according to this model will follow equation 12.4.3. To apply the model to the absorbance λ of a specific molecule we need to determine N (number of \pi electrons) and ℓ (length of the conjugated chain).

Number of π electrons in cyanine dyes (N): In the chain between the two nitrogen atoms, each carbon atom contributes one π electron. The π system also includes a total of three additional electrons contributed from the N atoms. Two of these electrons are contributed from the neutral N, while one is contributed from the cationic nitrogen (assuming the resonance structures shown in Figure 12.4.2). If we denote the number of carbon atoms in the polymethine chain (between the two nitrogen atoms) by p, then N, the number of π-electrons, is p + 3.

$$N = p + 3 \tag{12.4.4}$$

Where N is the number of π electrons in the system, and p is the number of carbon atoms between the nitrogen atoms.

Approximation of ℓ in cyanine dyes: The total length of the potential well is taken to be the length of the shortest carbon chain between the nitrogen atoms *plus one bond length at each end*. Assuming that the length of one bond is 1.39×10^{-8} cm, an approximation for ℓ is

$$\ell = (p + 3)a \tag{12.4.5}$$

where $a = 1.39x10^{-8}$ cm is the mean distance between atoms in the chain.

PIB model for Cyanine Dyes: Substituting 12.4.4 for N and 12.4.5 for ℓ in equation 12.4.3 yields:

$$\lambda = \frac{8mca^2}{h}\frac{(P+3)^2}{P+4} \tag{12.4.6}$$

If polarizable groups are present at the ends of the chain, then the potential energy of the π-electrons in the chain does not rise so steeply at the ends. This results in lengthening of the box length, ℓ, which can be incorporated into equation 12.4.6 through the addition of a new "lengthening" parameter, γ, resulting in

$$\lambda = \frac{8mca^2}{h}\frac{(P+3+\gamma)^2}{P+4} \tag{12.4.7}$$

where γ should be a constant for a series of dyes of a given type and should lie between 0 and 2. If such a series is studied experimentally, the empirical parameter γ may be adjusted to achieve the best fit to the data.

The Hückel Molecular Orbital (HMO) model

The molecular orbital (MO) energy level diagrams of a conjugated π- system can be constructed using a set of approximations suggested by Erich Hückel. The Hückel Molecular Orbital (HMO) method is not traditionally approached as an ab-initio quantum calculation (from theory alone), but is usually used as an empirical method (includes experimental data) for doing quantum calculations. This means that some number of adjustable parameters appear in the theory, and these parameters are determined by comparison with experiment (such as the electronic spectra of dye molecules). If the theory is successful, it can be used to predict the spectra and properties of other conjugated systems once the values of the adjustable parameters have been set for some set of reference compounds.

The Hückel model assumes that a π-molecular orbital, Ψ, delocalized over n atoms can be written as a linear combination of n atomic orbitals (LCAO) ϕ_i

$$\Psi = \sum_i c_i \phi_i \tag{12.4.8}$$

where the ϕ_i's are the atomic p_z orbitals on the atoms i (z is perpendicular to the molecular plane). The corresponding one-electron π density at atom i is given by

$$\rho_{i\pi} = c_i^2 \tag{12.4.9}$$

The energy E and the coefficients c_i for the ground state are determined by use of the *variation principle*, which says that one should choose the coefficients such that

$$E = \frac{\int \Psi H \Psi d\tau}{\Psi^2 d\tau} = minimum \tag{12.4.10}$$

Here the Hamiltonian, H, is an effective one-electron energy operator whose explicit form need not be specified in the empirical HMO approach. The variation principle ensures that the lowest-energy state is as close as possible to the true energy, and the coefficients are obtained from the minimization relations

$$\frac{\partial E}{\partial c_i} = 0; \quad i = 1 \ldots n \tag{12.4.11}$$

This results in n equations of the form

$$\begin{array}{cccc} c_1 (H_{11} - S_{11}E) + & c_2 (H_{12} - S_{12}E) + & \ldots & c_n (H_{1n} - S_{1n}E) = 0 \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ c_1 (H_{n1} - S_{n1}E) + & c_2 (H_{n2} - S_{n2}E) + & \ldots & c_n (H_{nn} - S_{nn}E) = 0 \end{array} \tag{12.4.12}$$

In these equations, $H_{ii} = \int \phi_i H \phi_i d\tau \equiv \alpha_i$, called the ***Coulomb integral***, is the energy of an electron in a 2p orbital on atom i, while $H_{ij} = \int \phi_i H \phi_j d\tau \equiv \beta_{ij}$, the *resonance* or ***bond integral***, represents the interaction energy of two atomic orbitals on atoms i and j. Both α_i and β_{ij} are negative energy quantities. $S_{ij} = \int \phi_i \phi_j d\tau$ is the overlap integral, which, in the simplest approximation, is taken to be 1 if i = j, and 0 otherwise. For a π system involving only carbon atoms, $\alpha_i \equiv \alpha$ and Equations 12.4.12 take the form

$$\begin{array}{cccc} c_1 (\alpha - E) + & c_2 \beta_{12} + & \ldots & c_n \beta_{1n} = 0 \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ c_1 \beta_{n1} + & c_2 \beta_{n2} + & \ldots & c_n (\alpha - E) = 0 \end{array} \tag{12.4.13}$$

These equations have a nontrivial solution only if the corresponding ***secular determinant*** vanishes:

$$\begin{vmatrix} \alpha - E & \beta_{12} & \dots & \beta_{1n} \\ . & & & . \\ . & & & . \\ . & & & . \\ \beta_{n1} & \beta_{n2} & \dots & \alpha - E \end{vmatrix} = 0 \tag{12.4.14}$$

The HMO method makes several simplifying assumptions. The first of these are as follows:

1. The π-orbitals are considered separately from the σ-orbitals. The σ-orbitals only enter indirectly in so far as they determine the geometry of the molecule.

2. Treat all the carbon atoms as identical. This means that all the Coulomb integrals (α) are equal.

The next stage is to express the π-orbitals as LCAOs of the C2p-orbitals, ϕ. In ethene (CH_2=CH_2) we would write

$$\Psi = c_A(\phi_A) + c_B(\phi_B) \tag{12.4.15}$$

and in butadiene (H_2C=CH−CH=CH_2)

$$\Psi = c_A(\phi_A) + c_B(\phi_B) + c_C(\phi_C) + c_D(\phi_D) \tag{12.4.16}$$

The optimum coefficients and energies are found by the variation principle. This involves solving the secular determinant, equation (Appendix B.7), which for ethene would be

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{12.4.17}$$

and its roots are $E = \alpha \pm \beta$. The state with energy $\alpha + \beta$ corresponds to the bonding combination (β is negative) and $\alpha - \beta$ corresponds to the antibonding combination, Figure 12.4.1.

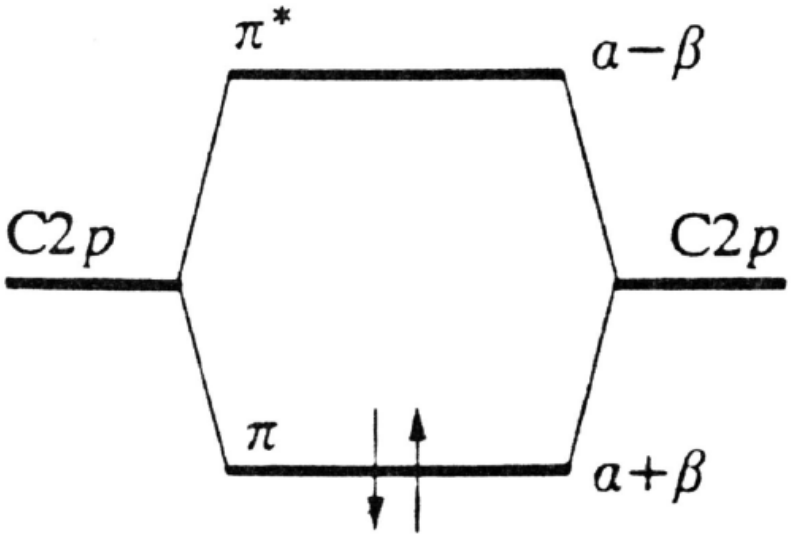


Figure 12.4.1: The Hückel Molecular Orbital Energy Levels of Ethene. Two electrons occupy the lower π-*orbital*. (CC-NC-BY-DUKE CHEM)

Each carbon atom supplies one electron to the π-system and the bonding orbital is occupied by an electron pair. The π-electronic energy of ethene is therefore $2\alpha + 2\beta$. The excited state of the molecule, when an electron is excited into the π^*-orbital, lies about 2β above the ground state.

In the case of butadiene, the approximations result in the determinant

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{12.4.18}$$

This expands into the quadratic equation

$$x^4 - 3x^2 + 1 = 0; \quad x = \frac{(\alpha - E)}{\beta} \tag{12.4.19}$$

with roots x^2 = 2.62, 0.38. Therefore, the energies of the four LCAO-MOs are

$$E = \alpha \pm 1.62\beta \quad and \quad E = \alpha \pm 0.62\beta \tag{12.4.20}$$

as shown in Figure 12.4.2. There are four electrons to accommodate, and so the ground state configuration is $1\pi^2 2\pi^2$.

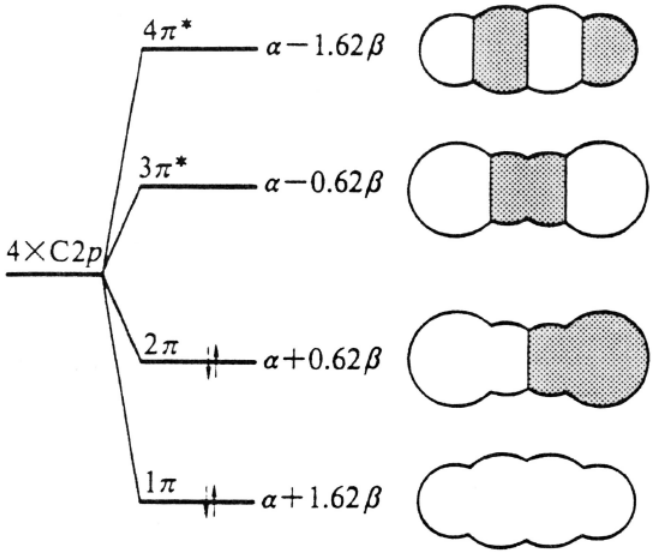


Figure 12.4.2: The Hückel molecular orbital energy levels of butadiene and the top view of the corresponding π-orbitals. The four p-electrons (one supplied by each carbon atom) occupy the two lower (\pi \)-orbitals. Note that the orbitals are delocalized. (CC-NC-BY-DUKE CHEM)

An important point emerges when we calculate the total π-electron binding energy in butadiene and compare it with what we find in ethene. In ethene the total energy is $2(\alpha + \beta) = (2\alpha + 2\beta)$; in butadiene it is $2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = (4\alpha + 4.48\beta)$. Therefore, the energy of the butadiene molecule lies lower by $(4\alpha + 4.48\beta) - 2(2\alpha + 2\beta) = 0.48\beta$ (roughly –36 kJ mol^{-1}) than the sum of two π-bonds. This extra stabilization of a conjugated system is called the ***delocalization energy.***

To obtain the wavefunction for a given energy state, E_j, one substitutes E = E_j into Equation 12.4.13 and solves for the jth set of coefficients c_{j1}, c_{j2}, ..., c_{jn}. This process actually gives only ratios of coefficients; to determine numerical values, we add the normalization condition

$$\int \Psi_j^2 d\tau = \sum_i c_{ij}^2 = 1 \tag{12.4.21}$$

The four Hückel molecular orbitals for 1,3-butadiene are

$$\begin{aligned} \Psi_1 &= 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \\ \Psi_2 &= 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4 \\ \Psi_3 &= 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4 \\ \Psi_4 &= 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4 \end{aligned} \tag{12.4.22}$$

In addition to π-electron energies and wavefunctions, the HMO approach also allows one to calculate several other quantities of chemical interest, such as electron densities, bond orders and free valence.

Heteroatoms

Heteroatoms (X) may be incorporated in the HMO method by appropriate changes in the empirical α and β parameters associated with each atom and bond. A common example would be the inclusion of the π-electron contribution from the nitrogen atom in pyridine. These changes are incorporated in units of the standard α_0 and β_0, usually of benzene, by use of the definitions

$$\alpha_X = \alpha_0 + h_X \beta_0 \tag{12.4.23}$$

$$\beta_{CX} = k_{CX} \beta_0 \tag{12.4.24}$$

Calculations involving such changes can be made by solving the secular equations. Unfortunately there remains considerable controversy concerning the specific values to be used for the h and k-parameters of various heteroatoms. Part of the problem is that there are several variations of MO theory and each will yield somewhat different parameter values with a given application.

We should distinguish, for example, the nitrogen in pyridine from a pyridinium nitrogen. In the former case, the heteroatom contributes two electrons to the π-system; in the latter case it contributes one. In the second part of the analysis of your experimental data, you will use a "canned" HMO computer program to determine the energy levels and molecular orbitals of the π-states of the dye molecules (as a function of β). By comparison of these results with your experimental data, you will determine an empirical value for β. Note that this program incorporates values for the heteroatom parameters h and k. You will need only to specify the location and type (e.g., pyridine-type nitrogen) of each heteroatom in the molecule to be studied.

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12.5: Hückel Calculations Using Hulis (Part II)

The ELN template for this part of the experiment is here: ELN01_2_Huckle2022.docx

Huckle Calculation Tasks

Perform the tasks listed here using the instructions for using Hulis that are given below.

1. Perform Huckle Molecular Orbital (HMO) calculations for each of the four dyes. In the HMO analysis, omit the ethyl groups since they are not part of the conjugated network. Save a screen-shot image of the entire program window showing the structure and the orbital diagram before moving on to the next one.
2. Calculate the energy difference, ΔE, between the HOMO and LUMO levels (in terms of β) for each dye.
3. Plot the experimentally observed ΔE's (kJ/mol) (from UV-vis in Part I, plot as y or ordinate) vs the calcuated HMO ΔE's (abscissa or x).
   a. From the least-squares slope of the resultant line, determine a semiempirical value for β (β is the spectroscopic exchange integral). Report the uncertainty in β.
   b. Compare your derived value of β with the accepted range for this constant (a.k.a spectroscopic exchange integral), which is – 250 to – 350 kJ/mole.[9]
4. Use your value of β to calculate the energy difference, ΔE, between the HOMO and LUMO levels in units of kJ/mol and eV for each dye. Using these energies, calculate the wavelength (nm) at which you would expect to observe this HOMO → LUMO transition for each dye, using the HMO model.
5. Calculate the percent error between your calculated HMO results your experimental values. Tabulate your data in the format shown below.

	WAVELENGTH (nm)						
Dye #	λ_{max} Literature*	λ_{max} Experimental		λ_{max} Particle-in-box		λ_{max} HMO	
		Value (nm)	Absolute Error (nm)	Value (nm)	% Error (from exp.)	Value (nm)	% Error (from exp.)
		±					
		±					
		±					
		±					

* reference for your literature values goes here

6. Use this table as the basis for discussion of your results. Which theoretical model gives the best fit to the experimental data, and why? Are the results for each dye equally satisfactory? If your answer is no, explain why you think this is so. How are these models useful and what might be done to improve the results?
7. Calculate the wavelength (nm) and minimum excitation energy (eV) of the molecule CH2=CHCH=CHCH=CHCH=CH2 using the HMO model program. In calculation use your value of β to convert to electron volts. What color does the molecule absorb from white light? What color does it then appear?

Instructions For Using The Program "Hulis" ver. 3.0.x

Note

Hulis is a Java applet. Java must be installed to run the applet. You are welcome to run it from your own laptop if Java is installed. But for your convenience in the event that you do not want Java on your computer, the program is available on all of the lab computers.

Hulis and Java can be downloaded here: Huckel Theory and HuLis

1. Double-click on the Hulis icon to Start the Program
2. Running the Program:
   The main screen shows a molecule builder. Highlight **Build** on the left side of the screen if it is not already highlighted when the program starts.

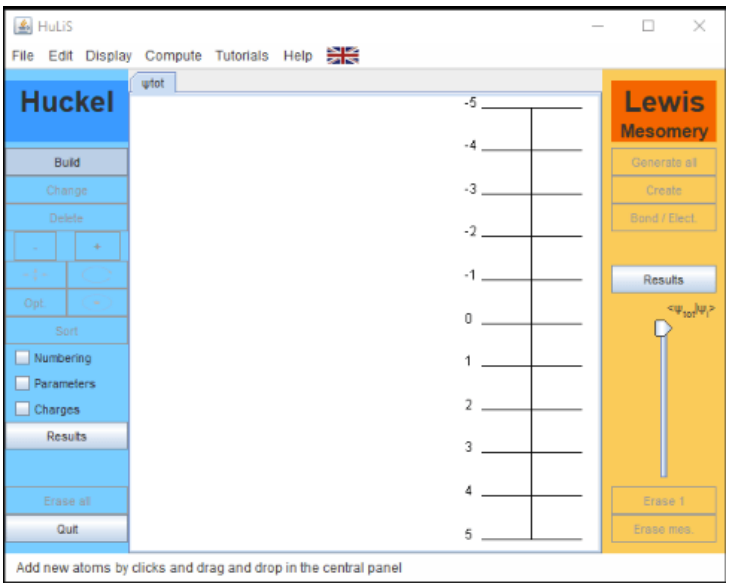
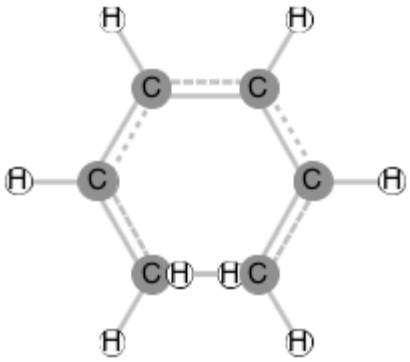
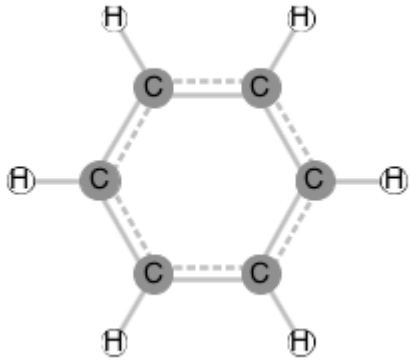


Figure 12.5.1: The Hulis Main Screen. (CC-NC-BY-DUKE CHEM)

To build a molecule, for example, Dye 1, begin by clicking anywhere in the blank window in the center of the screen. A CH_3 group should appear. Click on one of the available hydrogens to add a conjugated carbon to your molecule. As you add carbons to form the first ring, you will see the orbital diagram for the molecule appear in the right-hand panel of the program.



You can follow the electron count from this pane of the program window. After putting 6 carbons to form the ring, you will need to form a bond between the two open and adjacent carbons. To do this, simply click on one of the open carbons and drag a bond over to the adjacent open carbon. The hydrogens will disappear and a delocalized C-C bond will form.



3. Continue adding carbon atoms as appropriate to form the template molecule. When you are done your structure will look like this:

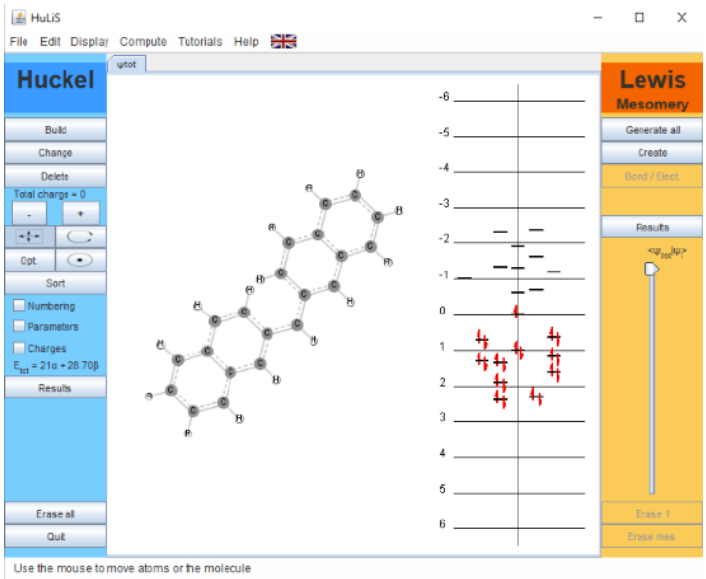
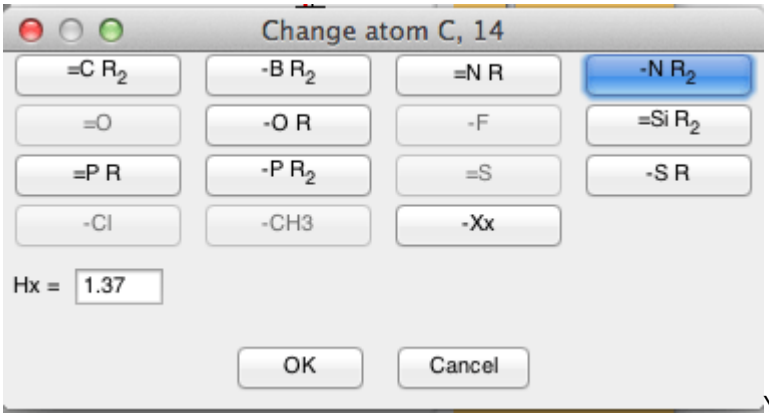


Figure 12.5.2: Dye 1. Note that for the purposes of a Hückel calculation the ethyl groups are omitted (CC-NC-BY-DUKE CHEM)

Note

You can rescale the display on the screen using Zoom out from the Display menu. You can also move, rotate, and center the molecule in the display window with the appropriate control buttons in the left-hand (blue colored) pane of the program window. In the image above the Move button is currently highlighted.



4. You now need to change two of the carbon atoms to nitrogen to complete the structure. Click on the Change button in the left-hand pane, and then double-click on the appropriate carbon in your structure. A Change Atom box appears. Select =NR to change this to the pyridinium group. Check to be sure the value in the Hx box = 0.51. Click on OK. Now change the other carbon to a nitrogen in the same way, but this time select the –NR2 option. Be Sure the value in the Hx box = 1.37. Click OK. Finally, make the molecule a cation by clickingh the + in the left-hand pane to increase the Total charge to 1. You final molecule will look as shown below.

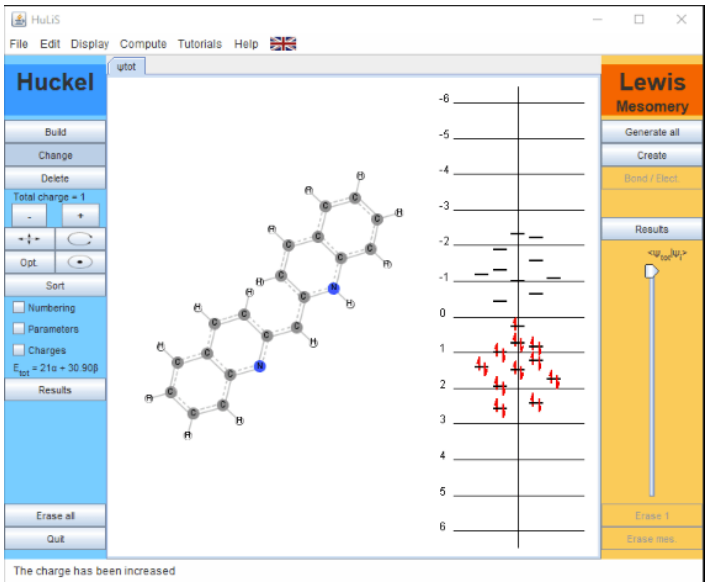
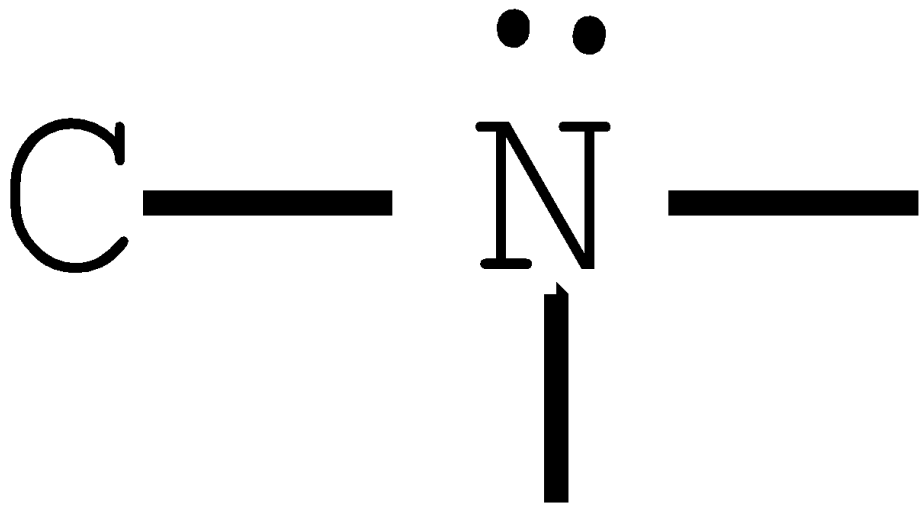
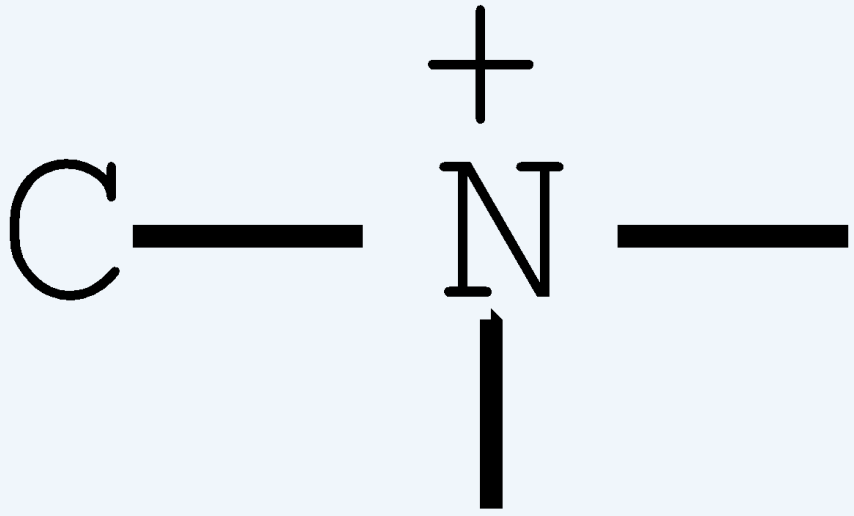


Figure 12.5.3: 1,1'-Diethyl-2,2'-Cyanine Iodide. The ethyl groups are omitted to simplify the calculations. (CC-NC-BY-DUKE CHEM)

Looking at the orbital diagram in the right-hand (orange) pane of the program screen you will see the occupied and unoccupied orbitals, as calculated by the simple Hückel approximation. You can see that the 21 pi-electrons in the molecule occupy the first 11 pi-orbitals; the HOMO to LUMO transition occurs between the 11th and 12th pi-orbital.

5. Click on the Results button, and a Results window appears with significant information about the Hückel calculation. Please note the following things:
   a. As you scan down the Hamiltonian matrix check to see that the Coulomb and Exchange integrals for heteroatoms and carbon-to-heteroatom bonds are as shown in the table below. If you need to see how your atoms are numbered in your structure to make it easier to find them in the Result table, put a check in the Numbering box in the left hand pane of the program window.

Atom	Bond		Nu of p- Ele
C	C=C		1
N		Pyridine	2
N		Pyridinium	1

b. In the Orbitals section of the Results box count over the appropriate number of orbitals (11 in the case of Dye 1), and record the results for the HOMO and LUMO in this molecule.

2- Orbitals :					
εi :	α + 2.5600β	α + 2.4065β	α + 1.9386β	α + 1.7503β	α + 1.4876β
α + 1.3928β	α + 1.2322β	α + 1.0000β	α + 0.8229β	α + 0.7227β	α + 0.2737β
α - 0.4390β	α - 0.6513β	α - 1.0000β	α - 1.0928β	α - 1.1960β	α - 1.3237β
α - 1.5793β	α - 1.8803β	α - 2.2244β	α - 2.3204β		

Figure 12.5.4: Orbital Energies for Dye 1. (CC-NC-BY-DUKE CHEM)

Notice that in this case the energy of the HOMO is $\alpha + 0.2737\beta$; and, the energy of the LUMO is $\alpha - 0.4390\beta$.

Note

NOTE: you can change the number of digits in the display from **Preferences**, under the **File** menu.

Close the Results Box.

c. To get a visual representation of the pi-molecular orbitals generated in the Hückel program, simply click on one of the orbitals in the right-hand pane of the program window. The orbital will appear on top of the molecule in the main screen. The image below is of the HOMO.

You can turn off the orbital display from your molecule by clicking below the orbitals in the right-hand pane of the program window. Save a screen-shot image of the entire program window showing the structure and the orbital diagram.

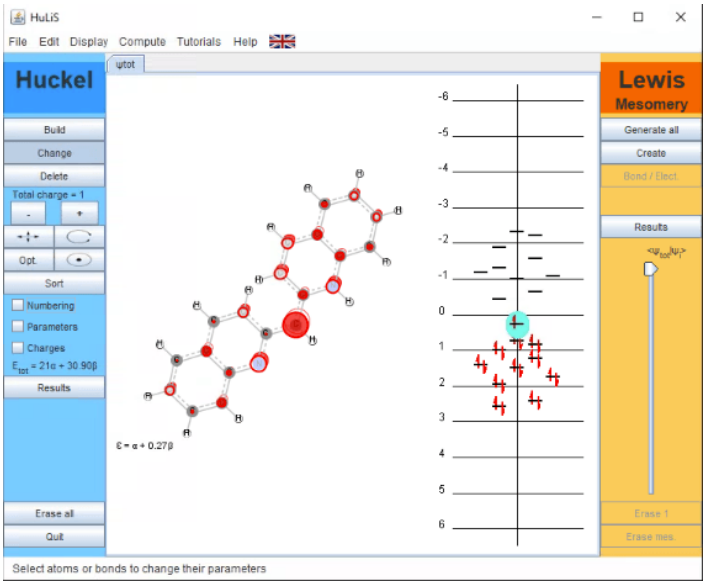


Figure 12.5.5: The Highest Occupied Molecular Orbital in Dye 1. (CC-NC-BY-DUKE CHEM)

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12.6: Introduction to Particle in a Box applied conjugated molecules

Definition: Conjugation

A conjugated π system is one that contains alternating single and double or triple bonds along a chain of carbon atoms. The most common type of conjugation is alternating double and single bonds. A simple example is the butadiene molecule. $H_2C{=}CH{-}CH{=}CH_2$

The Particle-In-A-Box approximation

Electrons in the π-electron system of a conjugated aromatic compound are not restricted to specific nuclei but are free to move throughout the system. In a linear conjugated system the potential energy of the electrons will vary along the chain, being lowest near the nuclei and highest between them. To a first approximation, however, it can be assumed that the potential energy of the electrons is constant along the length of the chain and increases to infinity one bond distance beyond the end atoms of the chain. The electrons may be visualized as being contained in a one-dimensional potential well, of length ℓ, and occupying orbitals of different energy within the well. The wave functions representing the orbitals and the energy levels of the orbitals can be obtained by solving the Schrödinger equation for this system.

For a one-dimensional system the Schrödinger equation takes the form

$$\frac{\partial^2 \psi_{(x)}}{\partial x^2} + \frac{8\pi^2 m}{h^2}\left(E - V\right)\psi_{(x)} = 0 \tag{12.6.1}$$

where $\psi_{(x)}$ are wavefunctions that satisfy the equation (eigenfunctions), E is the energy of the particle of mass m, V is the potential energy, and h is Planck's constant.

The potential energy, V, is a constant within the well of length ℓ, where $\psi_{(x)}$ must vanish for $x \leq 0$ and $x \geq \ell$ and $V = \infty$. This allows us to conveniently set V equal to zero in the region $0 \leq x \geq \ell$ when deriving solutions of the equation. The equation then reduces to

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2 \psi_{(x)}}{\partial x^2} = E\psi_{(x)} \tag{12.6.2}$$

Solutions of this equation are $\psi_{(x)} = A \cdot \sin\left(\frac{n\pi x}{\ell}\right)$, where A is a constant and n = 1,2,3,... etc.

Verification that this wave function is indeed a solution of the Schrödinger equation may be obtained by substitution into the left- and right-hand sides of the above equation.

$$\begin{aligned}\text{Left-hand side} &= \frac{-h^2}{8\pi^2 m}\left(\frac{-n^2\pi^2}{\ell^2}\right) A \cdot \sin\left(\frac{n\pi x}{\ell}\right) \\ &= \frac{-h^2}{8m\ell^2} A \cdot \sin\left(\frac{n\pi x}{\ell}\right) \\ \text{Right-hand side} &= EA \cdot \sin\left(\frac{n\pi x}{\ell}\right)\end{aligned}$$

The function $\psi_{(x)}$ is a solution of the Schrödinger equation when the energy E of the system has the values $E = \frac{n^2 h^2}{8m\ell^2}$. The allowed energy levels are depicted diagrammatically below.

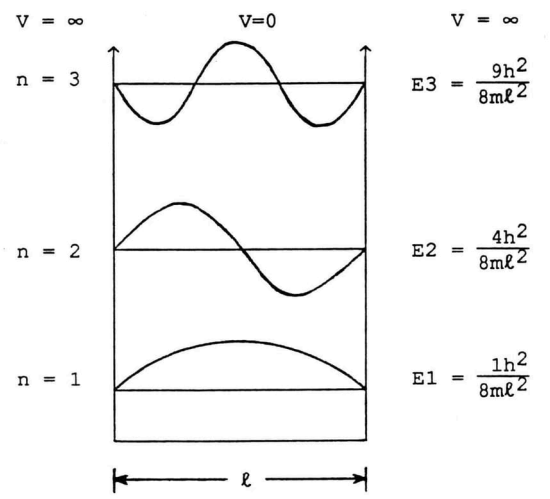


Figure 12.6.1: The Particle-in-a-Box Model.

The ground state configuration for the conjugated system of a molecule is derived by allocating two electrons to each of the energy levels in accord with the Pauli exclusion principle. Thus, a molecule with Nπ electrons will have the N/2 lowest levels filled and all the higher levels empty. When the molecule absorbs UV-vis light, the energy absorbed is from an electron in the HOMO (where n = N/2) becoming excited to the LUMO where n = (N/2) + 1. The energy change, ΔE, for this transition is

$$\begin{aligned}\Delta E &= E_{\left(\frac{N}{2}+1\right)} - E_{\left(\frac{N}{2}\right)} \\ &= \frac{\left[\left(\frac{N}{2}\right)+1\right]^2 h^2}{8m\ell^2} - \frac{\left(\frac{N}{2}\right)^2 h^2}{8m\ell^2} \\ &= \frac{(N+1)\,h^2}{8m\ell^2}\end{aligned}$$

Since $\Delta E = h\nu = \frac{hc}{\lambda}$ where c is the speed of light and λ is the wavelength, then

$$\lambda = \frac{8mc}{h}\frac{\ell^2}{(N+1)} \tag{12.6.3}$$

Thus if ℓ is known, this relation can be used to calculate the wavelength maximum of the band representing the transition from the ground state to the first excited state in a π-electron system.

PIB model for cyanine dyes:

This Particle-in-th-Box model can be applied to carbocyanine dyes which may be represented, for example, by the resonance forms shown below for the 1,1'- diethyl-4,4'-carbocyanine (cryptocyanine) cation.

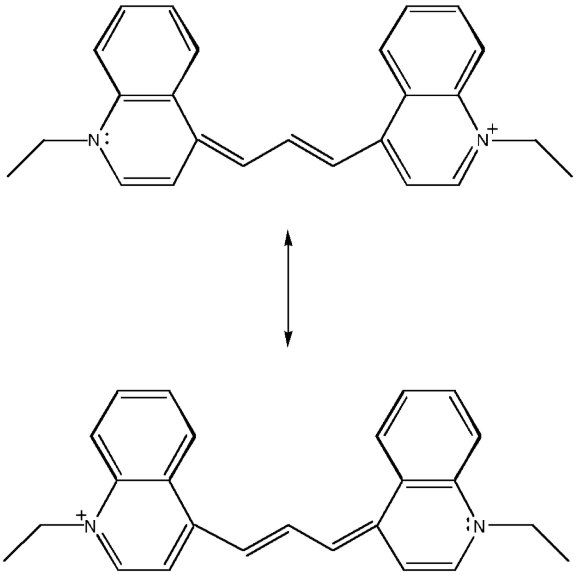


Figure 12.6.2: The *1,1'-Diethyl-4,4'-carbocyanine (cryptocyanine) cation*. (CC-NC-BY-DUKE CHEM)

The π-electrons in the molecule are regarded as a collection of "free" electrons (independent particles) confined to a box, whose wavefunctions are the square-well functions. Once again, these electrons are distributed among the wavefunctions and energy levels according to Pauli principles, so that the absorption of energy (light) according to this model will follow equation 12.6.3. To apply the model to the absorbance λ of a specific molecule we need to determine N (number of \pi electrons) and ℓ (length of the conjugated chain).

Number of π electrons in cyanine dyes (N): In the chain between the two nitrogen atoms, each carbon atom contributes one π electron. The π system also includes a total of three additional electrons contributed from the N atoms. Two of these electrons are contributed from the neutral N, while one is contributed from the cationic nitrogen (assuming the resonance structures shown in Figure 12.6.2). If we denote the number of carbon atoms in the polymethine chain (between the two nitrogen atoms) by p, then N, the number of π-electrons, is p + 3.

$$N = p + 3 \tag{12.6.4}$$

Where N is the number of π electrons in the system, and p is the number of carbon atoms between the nitrogen atoms.

Approximation of ℓ in cyanine dyes: The total length of the potential well is taken to be the length of the shortest carbon chain between the nitrogen atoms *plus one bond length at each end*. Assuming that the length of one bond is $1.39x10^{-8}$ cm, an approximation for \(\ell]) is

$$\ell = (p + 3)a \tag{12.6.5}$$

where $a = 1.39x10^{-8}$ cm is the mean distance between atoms in the chain.

PIB model for Cyanine Dyes: Substituting 12.6.4 for N and 12.6.5 for ℓ in equation 12.6.3 yields:

$$\lambda = \frac{8mca^2}{h}\frac{(P+3)^2}{P+4} \tag{12.6.6}$$

If polarizable groups are present at the ends of the chain, then the potential energy of the π-electrons in the chain does not rise so steeply at the ends. This results in lengthening of the box length, ℓ, which can be incorporated into equation 12.6.6 through the addition of a new "lengthening" parameter, γ, resulting in

$$\lambda = \frac{8mca^2}{h}\frac{(P+3+\gamma)^2}{P+4} \tag{12.6.7}$$

where γ should be a constant for a series of dyes of a given type. If such a series is studied experimentally, the empirical parameter γ may be adjusted to achieve the best fit to the data.

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12.7: Proceedure and Treatment of Data (Part I)

The ELN Template that can be used by your group during data collection for this part of the experiment is here: Dyes ELN Template

Please review the guidance on ELN templates.

This template is provided as a guide so that you know what data and information should be kept in a notebook. You may keep your notebook in any way you'd like, but it must be submitted in the form that is legible and can be submitted as a pdf on Gradescope.

Materials

- **Equipment:**
  - UV/Vis spectrometer (you will use either an Agilent Cary 60 Spectrometer or an Agilent Cary 100 Spectrometer)
  - Cuvettes (you will use glass cuvettes, which are optically transparent to visible (but not to UV) light)
- **Reagents:**
  - Reagent grade methyl alcohol (methanol)
  - Stock solutions of four polymethine dyes dissolved in methanol (solutions are approximately 10^{-4} M):
    - 1,1'-diethyl-2,2'-cyanine iodide
    - 1,1'-diethyl-2,2'-carbocyanine chloride (also known as pinacyanol chloride)
    - 1,1'-diethyl-2,2'- dicarbocyanine iodide
    - 1,1'-diethyl-4,4'-carbocyanine iodide (also known as cryptocyanine)

Note

The cyanine dyes used in this experiment are toxic irritants. Solutions of these dyes in methanol must be handled wearing gloves at all times. Perform all dilutions in a fume hood. Read the safety data sheets for these dyes (http://www.sigmaaldrich.com) prior to the lab.

Procedure

Determine Experimental λ_{max} from Absorption Spectra:

1. Perform instrument diagnostics tests using the Validate program. (See Operation Instructions for Agilent Cary Spectrophotometers)
2. Fill four standard glass cuvettes approximately 4/5 full with methanol (about 2.5 - 3 mL). Then add 3-15 drops of one dye to each cuvette. Add enough dye that you can see a light color for each solution.
3. Use the UV-vis to record the spectrum of each dye. If needed, adjust the solution concentration of one or more of the dye samples until the peak maximum absorbance reading is approximately 0.2 to 1.0 absorbance units.
4. Annotate the resulting overlay display of all four dyes, noting which dye is associated with each trace and the associated λ_{max} value.

Use Particle in the Box model to calculate theoretical λ_{max}

1. Determine γ for the series of homologous dyes.

   Use the Matlab script called ***dye_v3*** to determine the "best" value of γ This script will prompt you for information about the

four dyes, and the experimentally measured values of λ_{max}. It will solve the particle in a box equation for λ, separately for each dye, over the range of γ from 0.00 to 2.00 in steps of 0.01. It will sum the absolute deviation between the calculated λ and your experimentally measured λ_{max} for each value of γ, for each dye. It will output the one value of γ that produces the smallest summed deviation over the series of the four dyes. That is, the script will calculate the value of gamma which gives the best fit between peak wavelengths calculated using the free electron model and peak wavelengths measured experimentally. To use this script, start up a Matlab session and type the dye_v3 command:

```
dye_v3
```

Then simply enter the information as prompted by the script.

2. Use the output value of γ to calculate a value for λ_{max} for each of the four dyes using the equation

$$\lambda = \frac{8mca^2}{h}\frac{(p+3+\gamma)^2}{p+4} \tag{12.7.1}$$

(Remember that the value of the average bond length of a carbon-carbon bond, a, is 1.39 x 10^{-8} cm the mass of the electron, m, is 9.1 x 10^{-31} kg.)

Thinking about the Data

Be sure to address all of the following in your ELN.

1. **What is the experimental maximum wavelength for each dye solution?**
   Carefully examine all spectra (absorbance versus λ) and determine the wavelength of maximum absorbance (λ_{max}), for each dye. Enter your data with appropriate certainty in a data table in your ELN.
2. **What is the uncertainty in your experimental peak wavelength determinations?**
   Estimate error in each assignment of (λ_{max}) considering both the instrument tolerance indicated by the validation procedure (the wavelength accuracy test) and the data interval that was used during data collection.
3. **How do your results compare to literature values?**
   Compare your experimental results for λ_{max} with literature values for λ_{max} that you found as part of the pre-lab assignment.[10-12,14]
4. **What is the energy of electronic transition (absorption)?**
   For each dye, calculate the energy (eV and kJ/mol) of the *experimentally* observed λ_{max}.
5. **Determine γ for the series of homologous dyes.**
   Record the calculated value of γ in your ELN.
6. Calculate the **absolute error** between your experimental (from the spectrum) values and the literature values. Calculate both the absolute error and the percent deviation between your experimental (from the spectrum) and your calculated theoretical (Particle-in-a-box Model) λ_{max} results and record them in your notebook.
7. Tabulate your data in the format shown below.

		WAVELENGTH (nm)					
Dye #	Name of Data file	λ_{max} Literature*	λ_{max} Experimental		λ_{max} Particle in a Box		
			Value (nm)	Absolute Error (nm)	Value (nm)	Absolute Error (nm)	% Error

1			±				
2			±				
3			±				
4			±				
* reference for your literature values goes here							

8. Use the table above as the basis for a discussion of your results as follows:
   a. Compare your experimental λ_{max} values (from your spectra) with literature λ_{max} values. In your discussion, include a comparison of these λ_{max} values in the context of their absolute errors (the absolute error between your experimental result and the literature) and how that compares to the uncertainty (± value) of the measured and reported λ_{max} values.
   b. Compare the results of the Particle in the Box (PIB) model calculations of λ_{max} to the values derived from experiment.
      - As part of this comparison, discuss the agreement of computational to measured values in terms of the absolute error between computational and experimental values.
      - Also describe the relationship between λ_{max} and p for the measured λ_{max} values, and compare this trend with that of the computational results.
   c. Discuss how well the dyes fit into the trend described in part 8b. If they do not all fit the trend identified for a homologous series, explain why in the context of the PIB model and the structure of each dye.
   d. How is the PIB model useful and what might be done to improve the results?
9. Calculate the wavelength (in nm) and minimum energy (eV) of the molecule 1,3,5,7-octatetrene ($CH_2{=}CHCH{=}CHCH{=}CHCH{=}CH_2$) using the particle-in-a-box model. What color does the molecule absorb from white light? What color does it then appear to the eye?

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13: INTRODUCTION TO MATLAB

Learning Objectives

After completing the activities in this module, you will be able to

- Access and open MatLab
- Enter data sets on Matlab in the form of Matrices
- Perform simple mathematical operations using Matlab
- Plot data using Matlab
- Run a custom scripts using Matlab

Matlab is an interactive software package for scientific and engineering numeric computation. The name Matlab stands for *matrix laboratory*. Matlab works using essentially only one kind of object, a rectangular numerical matrix. In some situations, special meaning is attached to 1-by-1 matrices, which are scalars, and to matrices with only one row or column, which are vectors. Problem solutions are expressed in Matlab almost exactly as they are written mathematically - with no programming required.

In this laboratory course you will use Matlab to perform data analysis. The purpose of this activity is to review the basics of using Matlab and to show you a little of the power and graphics capability of this package.

13.1: Matlab Practice (In Class Activity)

13.1.1: The Basics

13.1.2: Practice with LiveScript

13.1.3: MatLab for Data Analysis In This Course

13.2: How to Access Matlab

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13.1: MATLAB PRACTICE (IN CLASS ACTIVITY)

Note

Before attempting these exercises, please make sure you have access to a working copy of the MatLab software and you have the custom scripts and binary files installed in the MatLab directory. If you are using FastX to access MatLab on campus, these files are already installed for you on the server. Otherwise, you should install MatLab and the custom files on your computer before proceeding.

The practice exercises in this module are meant to be completed during the scheduled meeting. The Matlab practice exercises are are designed to help you become literate in MatLab programing language and the MatLab GUI's so that you can accomplish the data analysis in this course. MatLab is the preferred tool for data analysis for the modules later in this lab semester.

Both of the activities below can be completed during the first laboratory meeting; collaboration among students is welcome, though each of you should complete the activity and submit your own work. Your work should be inspected by your teaching assistant (TA) before you submit the assignments and leave for the day. If your TA determines that you have done the activities correctly, you will receive full credit for this assignment.

13.1.1: The Basics

13.1.2: Practice with LiveScript

13.1.3: MatLab for Data Analysis In This Course

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13.1.1: The Basics

Originally Created by Lindsay Pederson, Fall 2022 | Modified by Kathryn Haas each semester since.

Caution

This exercise may be an uncomfortable experience if you haven't completed the basic MATLAB tutorials that were part of your pre-lab assignment. If you are feeling lost during this activity, please go back to the basic MATLAB tutorials to get comfortable with the basic commands and practice working with matrices before returing to this exercise.

MatLab General Layout

Open the MatLab program to begin. If the layout of your MatLab window looks different than the arrangement illustrated below, you can switch to the default layout using the "Layout" button in the Home Tab toolbar (see below). Choose "Default Layout" from the "Layout" drop down menu. If the layout still seems different than what is shown it might be because you have a Script or LiveScript file open in your MatLab program.

Compare your MatLab window to what is shown below. Read the figure below and familiarize yourself with the panels of the MatLab window. Then follow the instructions.

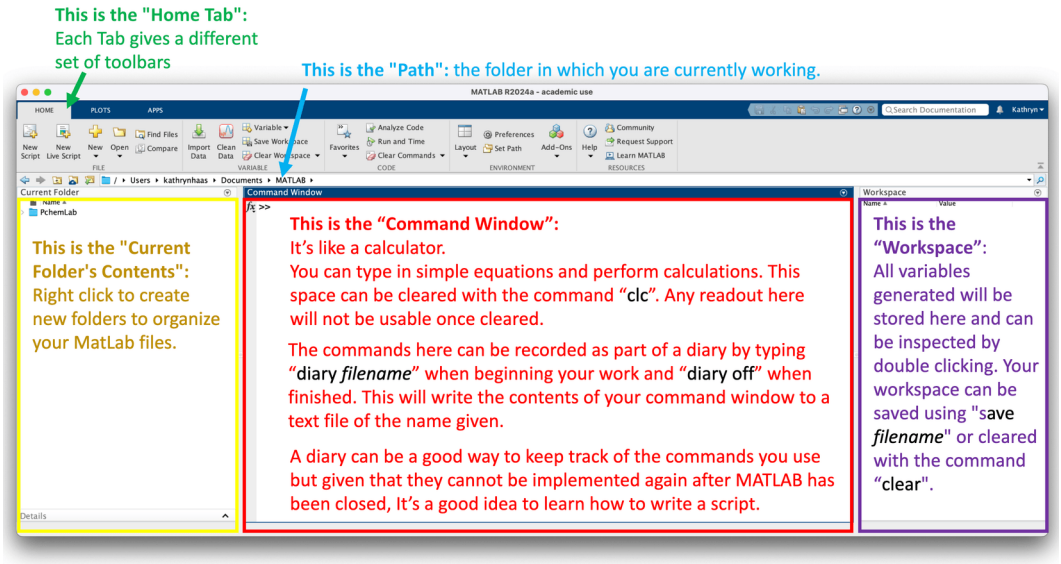


Figure 13.1.1.1: The default layout of the MatLab window (as of version R2024a). The tabs above the top toolar give access to different toolbar options. The file path is shown under the top toolar and indicates the current working folder. The Current folder's contents is shown in the pannel on the left. The center window is the Command Window, which functions like a calcuator. Type commands into the command window, save the work in the command window using the "diary filename" command to start saving and "diary off" when finished. All variables enterend in the Command Window will be populated in the Workspace, shown in the panel on the right. The Workspace can be saved using the "save filename" command or by using the "save workspace" button in the Home Tab toolbar. The workspace can be cleared using the "clear" command. (CC-NC-BY-SA; Kathryn Haas)

Practice with the Command Window

Find the command window in MATLAB. The command window is like a calculator. You can type simple equations here to perform calculations. The command window can be cleared by the command:

```
clc
```

All work is lost after the space is cleared.

The commands entered in the command window can be recorded in a text file (a diary). To record a diary, use the command "diary filename" at the beginning of your work:

```
diary filename
```

And then then at the end of the work:

```
diary off
```

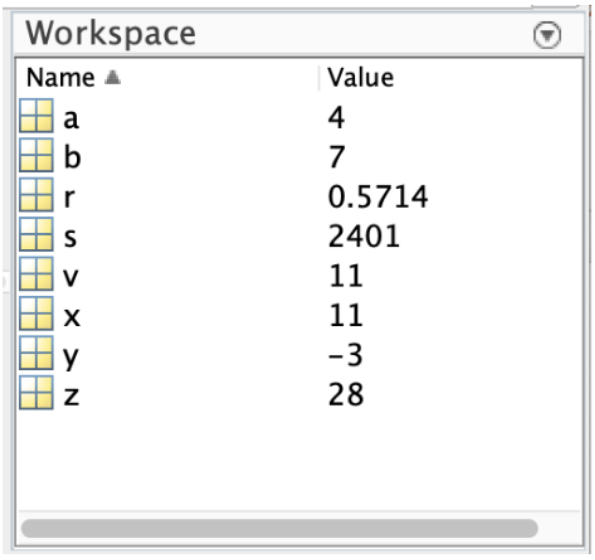
The diary file is a good way to keep track of commands, but the work cannot be implemented again from the diary file, so it has limited utility. **Script** and **Live Script** files are a much more useful way to record your work. **First, let's practice using the command window:**

Using the command window, begin a diary file with the name "practice_diary". Then do the following:

1. Clear the workspace by typing the clear command.
2. Create a variable *b* and set it equal to 7
3. Create a variable *a* and set it equal to 4
4. Add *a* and *b* and assign the result as *x*
5. Subtract *a* and *b* and assign the result as y
6. Multiply *a* and *b* and assign the result as *z*
7. Divide *a* by *b* and assign the result as r
8. Find *b* to the power of *a* and assign the result as s
9. Use the up arrow key to go back to the the command from step 4. Edit the command to assign it as *v* istead of *x* and end the command a semicolon; What does the semicolon do?
10. End the diary
11. Clear the command window with clc

The workspace

Notice that your workspace now contains all variables you defined. The workspace should look like this:



You can save the variables in the workspace as a binary ".mat file" with the command:

```
save filename
```

Use the command window to save your workspace using the file name "practice_workspace.mat". Notice the new file shows up in

the **Current Folder Window**.

Now, clear the workspace with the clear command.

```
clear
```

Just for practice, use the load command to load the file you just saved and inspect the workspace:

```
load filename
```

Clear the workspace again before moving to the next section.

Discussion Questions13.1.1.1

1. Where was the practice_diary file saved and what extension does it have? How would you submit a file like this to Gradescope?
2. When mathematical operations are performed in the command window, how are they defined in the workspace? What happens to the previous value in the workspace when you enter a new operation? (eq, try a + b , then a^b)
3. What does a semicolon at the end of a command do?
4. What does a percentage sign at the beginning of a line do?

Practice with Script Files

The Command Window is convenient for quick operations that you don't want to save. But it has some big limitations. For example, even if you do save the diary, you can't re-run any of the commands automatically. A better way to save your work is by entering it in a Script File.

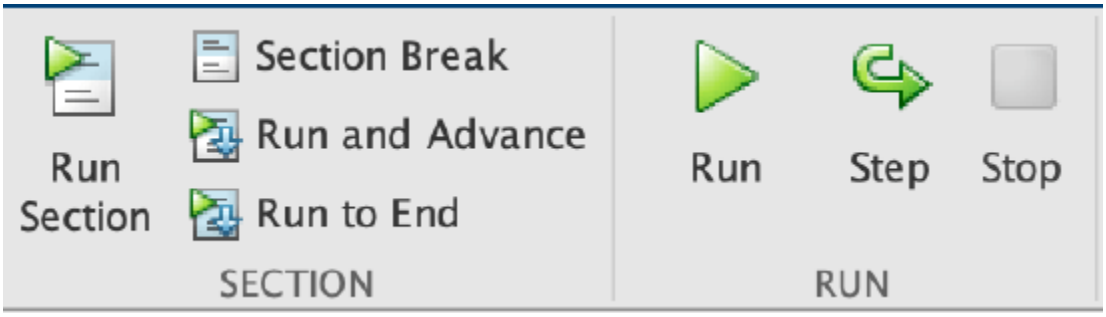
One way to start a new script is to go to the Home Tab and select **New**, then **Script**. Instead, let's use the command line to start a new script called "reference_script.m". Type the following into the command window:

```
edit reference_script.m
```

This will create a new script file. The new file should appear in the Current Folder window and it will open as a new tab in the Editor Window.

Find the Editor Window. In the Editor window, type the following:

```
%% Editor Exercises %%
% single percent sign indicates a text line
% double %% percent (only) indicates a section break.
% you can run each section of the editor by pressing the Run Section button.
% you can run the entire editor by pressing the Run button
```



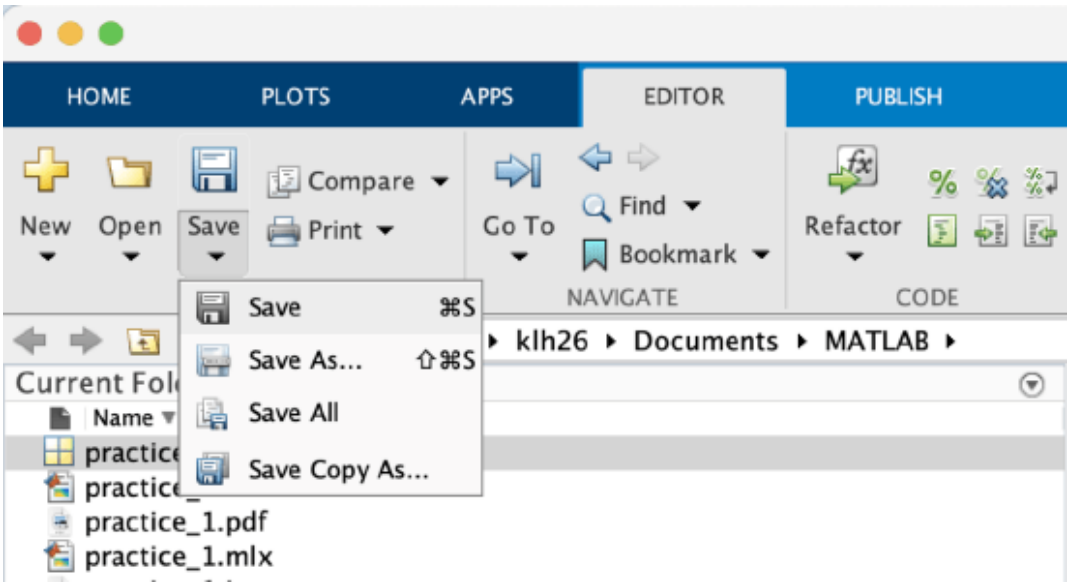

```
%%
%Type this into the new script in the Editor
b = 7
a = 4
```

```
% then hit run.
```

Notice what happens in the command window and in the workspace.

```
% again, type these examples of simple operations into the editor
x = a+b
y = a-b
z = a*b
r = a/b
s = b^a
% hit run and look at the command window
% then clear the command window and clear the workspace
% then add semicolons to the end of the lines and hit run again
```

Now that we see how the editor works, let's save the contents of the editor window as "reference_script.m". Go to the Editor tab and choose save.



At the end of the script that you just saved, add the following. Then run each section to see what happens. You can view any variables by typing their name in the command window.

```
%%
%% Building a reference sheet %%
a = 7;
b = 4;

%%
%Simple matrix - you can use spaces or commas to separate entries%
l = [1 2 3];
%%
%multiple rows - separated by semicolons%
m = [1;2;3];
%%
%matrices can have expressions in them%
n = [a+b, a-b, a*b];
%%
%transpose matrices with an apostrophe%
N = n';
%%
%multiply matrices
L = l*m;
M = m.*N;
```

```
%works the same with division
%%
%Create a matrix with regularly spaced intervals - defaults to one if not
%otherwise specified%
e = [1:16];
E = [1:0.5:16];
%%
%To reference specific elements of a matrix, call the matrix and then add
%coordinates (row, column) or just one number if it's a vector%
e7 = e(7);
m2 = m(2);
%%
%delete specific elements of a matrix
h = [1 2 3;4 5 6;7 8 9];
h(2) = [];
%check value of h in workspace
%%
%How to plot stuff
%you can just say "plot" but to intentionally keep track of figures it's a
%good idea to invoke figures by number
x = [1 2 3 4 5];
y = x.^2;
z = y./2;
figure(1)
hold on
plot(x,y)
plot(x,z,"o")
hold off
A = [1, 5, 0, 20];
axis(A)
xlabel('x')
ylabel('x^2')
title('Example')
%you can get help for any function you want to use (ex: plot()) by searching
%in the "Search Documentation" box at the top right of the screen
```

Save your files. Then clear the workspace and command windows before proceeding to the next section.

Discussion Questions13.1.1.2

1. What is the purpose of the period in the following statement? What happens if the period is removed?

   ```
   M = m.*N;
   ```

2. How can you delete the value 0.4 in the following matrix?

   ```
   mat1 = [0.1 0.2 0.3 0.4 0.5 0.9 1.0];
   ```

3. What does the "o" specification do in the code below:

   ```
   plot(x,z,"o")
   ```

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13.1.2: Practice with LiveScript

Install a custom script

The custom scripts (files with .m extension) and binary files (files with .mat extension) for this course are available here (click to go to GoogleDrive) using your Google account. If you are using the Chemistry Department *bohr* server to access Matlab, the scripts are already installed for you.

If you are using your own computer, the scripts and binary files should be added to the correct folder on your computer. Follow the instructions in this video to install the lsq script, which performs least squares analysis.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Practice using a custom script and a binary file

This is an exercise to give you some practice in using Matlab to analyze data provided in a binary file, and plot the results using a custom script for least squares analysis. Before you start, make sure the custom files lsq.m and expt-1.mat are in your working MatLab directory (see video above). The binary file "expt-1" simply contains pre-defined 80 x 1 vector matrixes "x" and "y". This is just to save you the hassle of typing in the values for each vector.

> Open the "Practice_LiveScript_XXX.mlx" file, and simply follow the instructions within the Live Script document.

The file linked above will walk you through the following steps to create a "final" plot.

1. Open the MatLab program and be sure that you are working in the directory containing the lsq script and expt-1 binary file.
2. Type the following: **load expt-1**
   Your workspace now contains two variables, x and y which obey the following relation:
$$y = Ae^{-Cx} \tag{13.1.2.1}$$
3. Plot y (ordinate) versus x (abscissa). Using Matlab, recalculate your data in linear form (ln y versus x) and plot the result. Using least squares analysis of the linearized data, calculate the values of A and C and report the standard deviation in these values. Using your calculated values of A and C, use Matlab to draw (a) the least-squares fitted line through your linear plot and (b) the best fit curve through your exponential plot. (NOTE: data should appear as points using the symbol 'o' and least squares fitted lines should be solid lines.)

   > **Expectation for a "final" full-credit plot in this course:**
   >
   > - Data is plotted in scatter format.
   > - Axes are correctly labeled, with correct units.
   > - When appropriate, a curve fit to the data is shown
   >   - equation of the line is shown on the plot, but not obscuring the data
   >   - uncertainty in slope and intercept provided

        - correlation coefficient (R) provided
    - Approrpate units are given for every value and every axis label.
    - Plot is centered on graph.
    - Text is easily readable (usually this means it is large enough to read easily.

4. You should show the plots described in (3) together with the values of A and C to your instructor. Each graph should have a title, and the x- and y-axes should be labeled.

This is an old video of this activity (before LiveScript files were developed.)

YouTube Video

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13.1.3: MatLab for Data Analysis In This Course

MatLab is the preferred tool for data analysis in this course. That means that we will provide MatLab templates for your data analysis in each module and we can provide some basic support for your computational work if you use MatLab. However, if you have a favorite tool that is not MatLab, you are welcome to use it instead from now on, but please know that your instructional team may not be able to offer technical support for other computational programs.

We provide the MatLab Live Script files that can support your work in the modules this semester. Let's take a close look at the one for your "Error Analysis" problem set (your next assignment, in Module 3).

With any time remaining in the class meeting, or with your time out of class, access the MatLab files for this course and find the "Treatment of Error folder". From this folder, open the file called "Error_StudentGuide_date.mlx" and follow the instructions within to begin completing your next assignment. Also proceed to the next module (Module 3) in this manual to view the pre-lab assignment for your next meeting.

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13.2: How to Access Matlab

There are two options for accessing Matlab at Duke:

1. You can access the Matlab program **using a lab computer.** However, Matlab is not installed on the lab computer hard drive. Rather, you can access the software that is installed on the chemistry department server (bohr) using an emulation software (FastX).
    - Alternatively, FastX is already installed on all laboratory computers in our P-Chem lab, and you are permitted to use those computers any time that the labs are open.
2. You can **download and install software onto your own computer** to access Matlab.
    a. Install FastX onto your own computer to access the Matlab installed on the chemistry department server.
    b. Install Matlab on your own computer.

The ability to access Matlab from your own computer will allow you to do your data analysis without having to come in to the lab computers. There are two ways that you might accomplish this. The first is to access the version of Matlab on the chemistry server, bohr, either by downloading and installing FastX (and the Duke VPN if you are off campus) onto your computer, or by using a browser-based version of FastX. The second is to download and install the actual Matlab program on your own computer. Both methods have advantages and disadvantages. Both the FastX and, if needed, VPN software packages are small and do not take up a lot of space on your computer. Additionally running the server version of Matlab through bohr gives you instant access to our in-house scripts that are used throughout the advanced lab classes. However, running a remote connection from your computer to bohr can result in a slower response since the speed will be related to the speed of your network connection. Installing the Matlab program on your own computer will likely give you a faster response, but the Matlab software will take up as much as six gigabytes of space. Additionally, you will have to get copies of our in-house scripts and place them in the Matlab path so that they can be used when needed. Instructions for both options are given in sections 1.1.2 and 1.1.3 of this Chapter.

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14.1.2.1: Welcome and Course Overview

👋 Welcome to CHEM 310L!

This laboratory course complements the undergraduate Physical Chemistry lecture sequence by giving students hands-on experience with instruments, techniques, and data analysis methods central to the field. Emphasis is placed on interpreting real experimental data and applying core physical chemistry concepts through guided inquiry.

The course is managed through Canvas, which hosts announcements, grading, instructor contact information, and assignment submission portals. The laboratory manual is hosted on LibreTexts and linked within Canvas. Because the manual is continually updated, students should always refer to the live LibreTexts site to access the most current version of each experiment.

Course Structure

This course consists of eight instructional modules, each focused on a major topic or technique in physical chemistry. You will work in collaborative groups to complete each experiment, analyze data, and interpret results. However, you will *write* your assignments independently and all work submitted for grading will be your own.

Assignments include:

- Pre-Lab Assignments – due the day of Lab Meeting by 1:00 PM
- Electronic Laboratory Notebooks (ELNs) – ELN's with completed discussion questions are due Sundays 11:59 PM after lab
- A final independent project – presented as an oral presentation

A detailed breakdown of points in each assignment is available in this google spreadsheet (Click).

Promoting Diversity, Inclusion, and Avoiding Harassment



All members of this course will foster an environment or listening and considering new ideas from a diverse group, with respect for all participants without regard to gender, race, ethnicity, color, sexual orientation, political orientation, age, religion, national origin, disability, or any other aspect of how we identify ourselves other than as fellow scientists.

There is zero tolerance in this course for any form of harassment or hate speech, during class meetings or outside of scheduled class time, which could include verbal or physical conduct that has the purpose or effect of interfering with anyone else's participation or performance, or of creating an intimidating, hostile, or offensive environment; any such harassment will result in dismissal from the course and will be reported to the college.

Duke University's Institutional Statement of Commitment to Diversity and Inclusion is found here (click):

"Duke aspires to create a community built on collaboration, innovation, creativity, and belonging. Our collective success depends on the robust exchange of ideas—an exchange that is best when the rich diversity of our perspectives, backgrounds, and experiences flourishes. To achieve this exchange, it is essential that all members of the community feel secure and welcome, that the contributions of all individuals are respected, and that all voices are heard. All members of our community have a responsibility to uphold these values."

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14.1.2.2: Assignment Details

Pre-Lab Assignments

To prepare for lab, you should do the following:

Wear Protective Clothing: As always, please dress appropriately for a laboratory environment. You must wear close-toes shoes and clothing must cover your body from your upper arms to your knees. You should also have your own pair of protective eyewear, bring them to lab, and wear them the entire time you are in lab. Safety eye wear can be purchased from the Graduate Chemistry Council (GCC). If lab attire is not jiving with your wardrobe, please purchase a lab coat and bring it with you so that you can cover up in lab. No student should be in lab without wearing protective eyewear and appropriate protective clothing.

Prepare by completing the Pre-Lab Assignment: It is absolutely essential that each student be prepared for lab meetings by reading the appropriate module in this manual, and completing the specified pre-laboratory assignments. The pre-laboratory assignments are designed to prepare you to operate efficiently and safely during the experimental module. You will not be allowed to conduct experiments if the pre-lab assignment is not completed before your lab meeting. If there is an extenuating circumstance that prevents your preparation, please inform your instructors as soon as possible.

The pre-lab assignment must be submitted as a single pdf document on Canvas at least 25 minutes before the scheduled lab meeting. Pre-lab assignments should be typed. If you prefer to write out equations by hand, they should be neat and inserted as an image in the appropriate place (please note that handwritten equations are only accepted for pre-lab assignments and ELNs, *but not for reports*). If you need advice for how to insert equations or images into your documents, please ask for help at least 48 hours before the assignment is due; an in-person (or zoom) meeting is most appropriate for this issue.

Late pre-laboratory work will not be accepted and will receive a score of zero. Your TA will evaluate the work and return it no later than the beginning of your lab section. Your preparedness will also be evaluated by your answers to oral questions pertaining to the laboratory from the TA and other lab instructors. The pre-lab and preparation accounts for 10 points of each experiment requiring a pre-lab.

For every experimental module there is a general pre-lab assignment and a specific pre-lab assignment.

General Pre-Lab Assignment (same for all modules)

Write a brief introduction to the experiment and the experimental plan using the following outline:

I. **Experiment Introduction:** In your own words, briefly describe the underlying theory and explain the principle upon which the experiment is based. Keep it concise; lengthy discussions or derivations of equations are unnecessary.
   a. Background (importance/relevance): A brief description and justification of the importance of the topic, *with references to source material*. What is the topic and why is it interesting and important? This is meant to "hook" the reader so they want to read about the topic.
   b. Theory: A concise paragraph or more describing the general theory for the method/technique used; this section should contain a reference to the appropriate pages of the textbook, or other source material from the literature.
   c. Goals/Purpose: Brief statement of purpose, which should indicate what is analyzed and the technique used. Limit to three to five sentences.

II. **Experimental Plan:** a short summary of the specific things that you would need to know in order to do the experiment without having access to your lab manual, with the understanding that you will always have a TA available to teach you how to use the instrument. The best way to approach this task is to thoroughly read the procedure for the experiment. While reading, take notes on the specifics of the work. What chemicals will you use? If you have to make solutions, what solutions do you need to make and of what concentration? How will you prepare them? What instrument will you use, and what specific instrument settings will you need to input (sometimes you will find this information in the Appendices that discuss the use of the instruments)? How many runs of each sample will you do; and over what wavelength, or temperature, etc. range? You do not need to write down how to use the instrument; we will teach you that. Bottom Line: we want you to write down only that pertinent information about samples, sample preparation, instrument and instrument parameters, numbers of runs, and other things, that you will need to know in order to do your work.

Specific Pre-Lab Assignment

Each module has a pre-lab assignment on the first page of the module. In general, each pre-lab assignment requires you read the entire module and write out the specified pre-lab assignments in your notebook before starting that laboratory work.

Electronic Laboratory Notebooks (ELNs)

Warning: Use cloud storage and backup

As you save your documents and develop systems of organizing your academic life, please learn to use a cloud server to automatically save and back up your work. Duke University supports cloud storage through Box and Microsoft tools. Google tools are also a free option. Proper use of these tools is expected. Please ask Dr. Haas if you need some instruction or recommendations for using these cloud-based tools to avoid loosing your work if/when computer hardware is lost or fails.

While we are aware that there are limited computer labs on campus, you also have access to computers also in the P-chem labs. Please plan to always complete your work 48 hours in advance so that any issues with your personal devices do not interfere with timely submission of assignments.

You will complete each experiment as a group, and there will be a dedicated instructor to answer questions. You will record observations using an electronic laboratory notebook (ELN); an example ELN template will be provided for each experimental module. The ELN will contain a written record of your group's activities during lab. Each student should collect a copy of the group data immediately after the lab meeting. Every P-chem lab computer has internet access, and you may either email data to yourself, save it using OneDrive, Google Drive, or Box, or collect it using a usb drive.

You will make the ELN your own by filling in your own work in the *Background*, *Theory*, and *Purpose* statements (from the pre-lab assignment). Edit these statements as necessary using the pre-lab assignment feedback from your instructor. The data collection should be done in your group. Then, do your own work to complete the questions and data analysis in the ELN. Your completed ELN must be submitted for grading before the end of the lab meeting. Extemtions may be given if extra time is needed to complete the data anaysis outside of the laboratory meeting. The maximum extension is up to the next scheduled meeting (~1 week). The pre-lab assignment accounts for 10 points, and the ELN accounts for 30 points for each experimental module.

Using the electronic laboratory notebook (ELN) template

Templates for each ELN will be provided as a guide to help you understand the minimum expectation for what should be recorded during the laboratory session. You should record all additional information and observations that you think is relevant. One member of the group should create a shared version of the ELN that will be used during the laboratory period, and in which all group members can contribute to the *Observations and Data* section. Then, each group member should make their own copy and complete the individual sections with their own work. ***To guard against the possibility of plagiarism, do not share an electronic copy of any ELN that contains your own work.***

There are three sections to each ELN: The "Observations and Data" section should be edited during lab while your group is working together. **The other sections must be written by you and should be *your own work*.**

Note

Before beginning any electronic laboratory notebook entry, track your changes. This way if you accidentally erase good data it can be retrieved afterwards. SAVE OFTEN when working outside the safety net of cloud-based autosave and backup.

- In Microsoft Word, select **Highlight Changes** from the Track Changes option under the Tools menu.
- In Google Docs, revision history is automatically saved as long as you are connected to the internet.

Pre-Lab section:

(Your own work) This is where you will copy/paste your own pre-lab work.

Observations and Data (Group data collection):

Record all observations and primary data as a group. This should include the actual procedure, instrument used, instrument tolerance (error), instrument settings, any notable observations, and all data collected during the lab period.

This section, in which you will have the same information as the rest of your group members, should contain only the information collected while in the laboratory. It should not contain your evaluation the data/observations in any way (that is the post-experiment work). If data are being collected by hand (handwritten on paper) it should be in clear, easy to read format. This handwritten data should be *immediately* entered into a shared ELN file. For data that are collected by a computer interface to your equipment, note the specific name of the data file in case you have to retrieve the file later! Take screen shots as necessary to capture important data to insert into the ELN. Write observations for each run, including "bad" or aborted runs, in a narrative style and state where the actual data file can be found (including filename) when needed.

Post-Experiment work:

(your own work)

Calculations of results and uncertainties: Unless otherwise instructed all calculations of results and uncertainties should be included as part of the laboratory notebook. In this course doing so will require the typing of a lot of mathematics. Please remember that you always have the option of writing your calculations out neatly on plain paper and scanning it to make a digital image that can be incorporated into an electronic notebook entry. Mathpix is recommended to help you convert equation images to Latex for insertion into typed documents (use the Free & Educational use option!).

Discussion of results: In this section you truly “think in the notebook”. Reflect on what you have done. Write this section in your own words after the observations are completed. Include charts, graphs (see below), tables or rearranged data and your rambling thoughts. Remember this is not a formal report. You want to be neat and complete, not necessarily a literary star. This section need not be long, but it should contain all pertinent information.

Graphs: Often you will generate graphs from your primary data files. They must be represented in this section of the laboratory notebook. It is not difficult to include digital copies of graphs within the electronic laboratory notebook, but you should remember that such images can easily make the file sizes large and thus difficult to work with. Below is a procedure that will work to include copies of your graphs in the notebook while minimizing the overall size of the resulting file. A reliable way to capture graphs/plots to insert into your lab notebook is to use WinSnap for PC (or screenshot on Mac). Each lab computer has WinSnap installed. You can take a screen shot by pressing SHIFT + COMMAND + S on the keyboard. This will allow you to select a region for capture and the image will be saved to the clipboard. Press CONTROL + V to paste. You can also open the WinSnap program from the desktop shortcut instead of using keyboard shortcuts. (SAVE OFTEN!)

Reports

In this course, ELN's that include answers to discussion questions (post-lab questions) are considered "reports" of your work.

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14.1.2.3: Academic Integrity

Academic Integrity vs Cheating

- **Academic integrity** means your work is an accurate representation of your own learning and understanding.
- **Cheating** or **academic dishonesty** occurs when your work misrepresents what you know, undermining your own learning and the trust that makes meaningful feedback possible.

Why Academic Integrity Matters in this Course

In this course, your written work is both a learning tool and an assessment tool.

- When you write, you articulate and refine your thinking.
- When we read your writing, your instructors and TAs see your reasoning, your decisions, and your conclusions. This allows us to give you feedback you can actually use to grow as a scientist.

You will also give and receive peer feedback. For that feedback to be meaningful — and for you to benefit from it — your work must reflect your own thinking.

Duke Community Standard

All students must adhere to the Duke Community Standard (DCS): Duke University is a community dedicated to scholarship, leadership, and service and to the principles of honesty, fairness, and accountability. Citizens of this community commit to reflect upon these principles in all academic and non-academic endeavors, and to protect and promote a culture of integrity.

To uphold the Duke Community Standard, students agree:

- will not lie, cheat, or steal in my academic endeavors;
- I will conduct myself honorably in all my endeavors;
- I will act if the Standard is compromised.

Regardless of course delivery format, itis the responsibility of all students to understand and follow all Duke policies, including academic integrity(e.g., completing one's own work, following proper citation of sources, adhering to guidance around group work projects, and more). Ignoring these requirements is a violation of the Duke Community Standard. Any questions and/or concerns regarding academic integrity can be directed to the Office of Student Conduct and Community Standards atconduct@duke.edu.

Using AI to Support Your Learning

AI tools (e.g., ChatGPT, Grammarly, Claude) can be powerful learning partners if you use them intentionally and transparently. But, if they are misused, these tools can undermine your learning.

Appropriate use of AI:

AI tools can play a valuable role in your learning process when used intentionally to coach you, or to help improve your writing.
You may use AI applications to:

- Improve organization and structure of your own writing using prompts like "*Revise this paragraph to improve clarity and structure, but keep the original meaning.*"
- Edit for grammar and clarity using prompts like "*Identify grammar errors and suggest fixed without changing the technical*

meaning of my writing."
- Refine your phrasing or writing style. "*Make this explanation appropriate for an audience of scientists outside my specialty.*"
- Brainstorming ways to present an idea you've already developed. "*Suggest alternative ways to phrase this description of my method.*"

After using AI in any of these ways, you must review, edit, and verify the output yourself. Be aware that AI tools can change the meaning of your words, and AI can hallucinate and give test that is not based in reality. You are responsible for ensuring that your final writing is clear, correct, and accurate —and that it represents your own learning, thoughts, and understanding.

Inappropriate use of AI:

Using AI to generate substantive scientific content — such as designing methods, interpreting data, or drafting analysis you have not developed or do not fully understand — is a misuse of these tools.

Examples of inappropriate use of AI:
- Generating new sections or paragraphs you did not develop yourself. (e.g., "Write an introduction section for a scientific manuscript about …")
- Asking AI to analyze your data or draw conclusions that you cannot explain (e.g., "Interpret my results and write the discussion section.")
- Rewriting entire drafts you did not author yourself.
- Fabricating sources, citations, or data.

Misusing AI in this way prevents your instructors and peers from providing meaningful feedback; it prevents you from learning and it wastes everyone's time.

A Quick Test: The "Could I Explain This?" Rule

Before submitting any work that involved AI, ask yourself:

- Could I explain every choice, result, and statement in my own words?
- Could I recreate the reasoning or analysis without AI's help?

If the answer is "no," then the AI use is likely inappropriate for this course.

When in Doubt, ask.

If you are ever unsure about whether an AI tool is supporting your learning appropriately, please ask a member of the instructional team. We are here to help you learn how to use these tools thoughtfully, responsibly, and always in service of your authentic growth as a scientist and writer.

Acknowledgements

Whenever you receive outside help—whether from a friend, a textbook, or an AI tool—you must acknowledge it. To help your instructors understand what kinds of support you are using and where you may need additional guidance, we ask that you clearly document all sources of assistance for each assignment.

Example of an Acknowledgements statement:

This statement on the responsible use of AI tools was created by Kathryn Haas for Advanced Lab Courses at Duke University. The statement was drafted with the support of OpenAI's ChatGPT. It draws inspiration from "AI with Intention: Principles and Action Steps for Teachers and School Leaders" by Tony Frontier and includes insights generously shared by Dr. Eliana Schonberg (Thompson Writing Program at Duke University).

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14.1.2.4: Lab Performance and Professionalism

A portion of the total available points for this course are allotted to your performance in lab. This includes an expectation for preparation before the lab period, arriving on time, using time effectively, performing the tasks well, contributing to the culture of safety, and helping to maintain a clean and safe environment. Your performance and professionalism in the lab is assessed through **Lab Citizenship points**.

🌟What does it mean to be a "Good Lab Citizen"?

Lab Citizenship refers to more than just following rules. It means self-regulating your behavior in a way that supports a safe, respectful, and productive lab environment—without needing constant reminders from instructors.

Your instructors are here to support your learning, not to act as the "lab police." We expect that you will take ownership of your space, your preparation, and your conduct. This includes not just compliance with safety policies, but also contributing positively to the shared environment, being considerate of others, and acting professionally.

Good Lab citizens:

- Arrive on time and ready to work
- Wear proper lab attire and PPE at all times without reminders
- Turn notifications off on electronic devices used during meetings
- Clean up after themselves and leave shared spaces better than they found them
- Use lab time effectively and help their group stay on track
- Label solutions, handle chemicals safely, and follow disposal protocols
- Respect the physical space, equipment, and people in the lab

When you do these things consistently, it frees your instructors to focus on helping you learn and grow as scientists — not on enforcing rules. Your Lab Citizenship grade score reflects your ability to self-regulate and contribute to a positive lab culture.

Lab Citizenship Checklist

Each Wet Lab session, you can earn 1 Lab Citizenship point by demonstrating professional, safe, and respectful lab conduct. This point is awarded as an “all-or-nothing” score based on the following expectations.



⚠️ Students **will not receive partial credit**—failure to meet any of these expectations may result in 0 points for the day.
*Distraction by electronic devices (messages, social media) during lab time is considered a violation of safety and using time well. You are advised to turn off notifications on electronic devices used during meetings.

Lab Citizenship Penalties

While Lab Citizenship is typically graded on a 1-point-per-session basis, certain behaviors may result in point deductions from your lab report score. These behaviors compromise safety, professionalism, or lab functionality and require stronger consequences.

Repeated or serious infractions will result in direct point deductions from your lab report grade for the corresponding module. The instructional team will notify you if a deduction has been applied and explain why. Some, but not all, examples are shown below:



⚠️ Repeated issues (e.g. forgetting goggles, being late, or poor cleanup) may also trigger **a conversation with the instructional team or department administrators** to resolve concerns and may result in failure of the course.

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14.1.2.5: Rubrics

The points that you earn during the semester will determine what letter grade you earn based on a traditional seven-point college grading scale.

$$\text{Letter Grade} \equiv \frac{\text{Points Earned}}{\text{Total Possible Points Earned}} \times 100 \tag{14.1.2.5.1}$$

Each of the modules and their components are allotted points based on the tentative information below. Teaching assistants will modify the point breakdown as necessary. These rubrics, and all changes to these rubrics, will be applied equally across all student's work in a given semester.

Overall points

Item	Point Breakdown	Total Points
Pre-semester Orientation Assignment	15	15
MatLab Pre-Lab MatLab In-Class Participation	10 25	35
Treatment of Error Pre-Lab Participation during In-Class Problem Session Accurate and Complete Problem Set	10 5 25	40
Absorption Spectra of Dyes Pre-Lab Absorption Spectra of Dyes ELN (including participation)	10 30	40
Electronic and Vib. Spectroscopy of Iodine Pre-Lab Electronic and Vib. Spectroscopy of Iodine ELN	10 30	40
Rotovibrational Spectroscopy (FTIR) Pre-Lab Rotovibrational Spectroscopy (FTIR) ELN (including participation)	10 30	40
Computational Pre-Lab Computational ELN	10 30	40
Individual Projects	50	50
TOTAL		300

ELN Point Deductions and other penalties for repeated issues

Issue	Typical deduction
Tardy by between 7 - 15 minutes	- 5 points to ELN *or* is not allowed not participate
Tardy by 16 - 20 minutes	- 10 points to ELN *or* is not allowed not participate
Tardy by more than 20 minutes	- 15 points *and* is not allowed to participate
Failure to wear safety eyewear in lab	- 5 points for each occur ance after first warning
Failure to dress appropriately to lab and must borrow clothing from instructors	- 10 points from ELN for each occurrence, or not allowed to participate
Displaying symptoms of illness and failing to wear a face mask during meetings	- 5 points for each occurrence

Detailed Rubrics for each module

MatLab

Introduction to MatLab	
10 points	Preparation for meeting by installing MatLab on computer, completing Matlab basics tutorials, bringing working computer with MatLab installed to lab meeting.
25 points	Participation in the MatLab Tutorial and correct completion of assignment.

Error

Treatment of Experimental Error	
10 points	Preparation for meeting by submission of attempt of all problems.
5 points	Participation in the Error study hall session
25 points	Correct response on all questions

Dyes with Huckle

Absorption spectra of conjugated Dyes	
10 points	preparation for lab (pre-lab assignment)
3 points	Spectra of the following: Validation of instrument, 4 dyes. Data: Uncertainty in peak wavelengths, comparison with literature values (See Q1-3)
2 points	Calculation of experimental Energy in eV from Λ_max (See Q4)
1 points	Selection of Γ using Matlab "dye" script (3 pts) and explanation of how dye script works (1 pt). (See Q5)
3 points	Calculate Λ_{max} from particle in the box model and compare with experimental value. (See Q6-7)
3 points	Discussion of results. (See Q8)
1 points	Calculation of Λ_{max} and Energy in eV for octatetraene. (See Q9)
3 points	HMO calculations for each dye; correct structures; # of π elecrons and connectivity matrix
2 points	Δ E (beta units) for each dye
2 points	MO diagram for each dye
3 points	Plot HMO ΔE vs observed ΔE, determine beta and uncertainty

Absorption spectra of conjugated Dyes	
2 points	Calculate energy difference in kL/mole, eV, and nm
1 point	completed table
3 points	Discussion: Which theoretical model gives the best fit to the experimental data, and why? Are the results for each dye equally satisfactory? If your answer is no, explain why you think this is so. How are these models useful and what might be done to improve the results?
1 points	Calculate the wavelength (nm) and minimum excitation energy (eV) of octatetraene using the HMO model program. In calculation use your value of β to convert to electron volts. What color does the molecule absorb from white light? What color does it then appear?

Iodine Spectroscopy (Electronic and Vibrational Coupling)

Students will participate in only one calorimetry experiment.

Iodine spectroscopy	
10 points	preparation for lab (pre-lab assignment)
PART I: Absorption spectrum	
1 point	Validation spectrum and calibrated absorption spectrum - peaks assigned
1 point	Plot delta G's vs (v'+1) with linear regression
2 point	Calculate w'e, X'e, D'e and a'
1 point	Comparison with literature
2 point	Uncertainty in w'e, X'e, and D'e
1 point	Q1: Determine value of v00
1 point	Q2: Why do the vibrational spacings get narrower as V(R) increases?
1 point	Q3: Why is the Morse potential asymmetric?
1 point	Q4: Why are some transitions called "Hot bands"?
1 point	Q5: How would you calculate X"e and D"e using the hot bands?
1 point	Q6: What are the units of the Morse parameter a?
Part II: Emission Spectrum	
1 point	Emission spectrum - peaks assigned
1 point	Plot deltaG" vs (v"+1) w/linear regression
2 point	Calculate w"e, X"e, and D"e
2 point	Uncertainty in w"e, X"e, and D"e
2 point	Calculate D"e using equation 8/ comparison with D'e
1 point	Calculate a"
1 point	Plot of V"(R) and V'(R) (morse in MATLAB)
2 point	Estimate R"e - R'e and R'e
1 point	Plot both V"(R) and V'(R) on the same graph (morse 2 in MATLAB)
1 point	Comparison with literature

Iodine spectroscopy	
1 point	Q1: Why are the vibrational spacings different in the ground and excited states?
1 point	Q2: Why is the shape of the Morse potential different in the ground and excited states?
1 point	Q3: How its it possible to observe emission peaks at higher energies than the pump energy?

FTIR

Rotovibrational spectroscopy of HCl/DCl using FTIR	
10 points	Preparation for meeting by submission of attempt of all problems.
17 Points for Part I	**Part I: HCL/DCl**
1 point	Spectra of HCl & DCl - assignments labeled; list of peaks (see Step 1)
2 points	Plot of $\tilde{\nu}_{(m)}$ vs m for 4 isotopes (see Steps 2 & 3)
5 points	$B_e, \alpha_e, \tilde{\nu}_o, I_e, r_e$, and k for each isotope (see Steps 4-8)
1 points	Comparison with literature value (1 points); parts a-c (3 points) (see Step/Q 9)
2 points	Ratios $\frac{\tilde{\nu}_o^*}{\tilde{\nu}_o}$ and $\frac{B_e^*}{B_e}$ for H, D, and $^{35}\mathrm{Cl}$ and $^{37}\mathrm{Cl}$ (see Step 10)
1 points	Explanation of why the ^{35}Cl /^{37}Cl isotope effect so much larger in DCl than it is in HCl (see Step/Q 11)
1 points	Application of Boltzmann populations of the ground-state levels to explain relative band intensities (see Step/Q 12)
1 points	Determination of relative abundance (see Step/Q 13)
2 points	Uncertainty in $B_e, \alpha_e, \tilde{\nu}_o, I_e, r_e$, and k for one isotope (see Step/Q 14)
1 point	Explanation of why we purge the FTIR spectrometer, and why we are careful to purge background and sample similarly (see Step/Q 15)
13 points for Part II	**Part II SO2**
1 point	Q1 Spec. of SO_2, vibrations labeled
2 points	Assign Bands
1 point	Compare to literature
2 points	Q2 other bands
2 points	Q3 k_1 and $\frac{k\delta}{l^2}$
2 points	Q4 C_v(vib) at 298 K and 500 K
1 point	Q5 Comp. of Spec. and exptl C_v\$
2 points	Q6 Uncertainty in k_1 and $\frac{k\delta}{l^2}$ (Q7)

Computational

Electronic Structure Calculations with Spartan	
2 point	Exercise I: Table summarizing HCl and DCl calculations
1 point	Exercise I: Comparison of computational results to experiment and literature data

Electronic Structure Calculations with Spartan	
1 point	Exercise I: Conclusions about the accuracy of the Hartree-Fock calculation
1 point	Exercise I: Analysis of bond lengths for HCl and DCl
2 point	Exercise II: C-O and C-H bond lengths; CHC and HCO bond angles
1 points	Exercise II: Comparison with literature
2 points	Exercise II: Calculation of energy difference between HOMO and LUMO
2 points	Exercise II: Images and descriptions of HOMO, LUMO, and other orbitals
3 points	Exercise III: Completed table
2 points	Exercise III: Comparison of computational results to literature
1 point	Exercise III: Evaluation of different theories/basis sets
2 points	Exercise IV: Completed table
2 points	Exercise IV: Comparison of computational λ_{max} to experimental and theoretical values
3 points	Exercise IV: Questions from Step 9
2 points	Exercise V: Equilibrium geometry energies of initial, transition, and final states
1 points	Exercise V: Reaction profile plots
2 points	Exercise V: Calculation of activation energy and ΔH

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14.1.3: INTRODUCTION TO MATLAB FOR PCHEM LAB

14.1.3.1: Pre-lab Assignment

14.1.3.2: Matlab Practice (In Class Activity)

14.1.3.2.1: The Basics

14.1.3.2.2: Practice with LiveScript

14.1.3.2.3: MatLab for Data Analysis In This Course

14.1.3.3: How to Access MatLab (Duke students)

14.1.3.3.1: Install Matlab on your own computer

14.1.3.3.2: Access MatLab Remotely Through FastX

14.1.3.3.2.1: Transferring Files Between Your Computer and Your Duke NetID Account

14.1.3.3.2.2: Access from off-campus (The Duke VPN)

14.1.3.3.3: Invoking Matlab From the Lab Computers

14.1.3.4: Using Matlab (Supplemental)

14.1.3.4.1: Linear Least Squares Analysis

14.1.3.4.2: Last Line Editing and Recall

14.1.3.4.3: Saving Data

14.1.3.4.4: Deleting Matrices

14.1.3.4.5: Quitting Matlab

14.1.3.4.6: Entering Matricies

14.1.3.4.7: Matrix Computation

14.1.3.4.8: Vectors

14.1.3.4.9: Subscripting

14.1.3.4.10: Finding, Deleting, Adding or Replacing Data

14.1.3.4.11: Output Format

14.1.3.4.12: The Help Facility

14.1.3.4.13: Array Operations

14.1.3.4.13.1: Array Addition and Subtraction

14.1.3.4.13.2: Array Multiplication and Division

14.1.3.4.13.3: Array Powers

14.1.3.4.13.4: Math Functions

14.1.3.4.14: Graphics

14.1.3.4.14.1: Basic Plots

14.1.3.4.14.2: Line Types

14.1.3.4.14.3: Multiple Plots

14.1.3.4.14.4: Manual Axis Scaling

14.1.3.4.14.5: Overlaying Plots

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14.1.3.1: Pre-lab Assignment

📅 **Due:** This assignment must be completed before 1:00 PM on your first lab meeting day (see syllabus schedule).

🕒 **Time:** Plan at least two hours to complete this assignment. If you run into technical challenges, this will take additional time.

🎯 **Purpose**: This pre-meeting assignment is designed to help you arrive to our first meeting prepared to complete course-specific MatLab training.

Pre-Lab assignment for MatLab

To prepare for the laboratory session on MatLab, please do the following prior to the laboratory period:

- Download and install MatLab on your personal laptop computer (see get access section).*
  - During MatLab Installation, select all of the following additional "Toolboxes":
    - Statistics and Machine Learning Toolbox
    - Curve Fitting Toolbox
    - Symbolic Math Toolbox
- Download the custom scripts and binary files (Get Scripts Here), and put these files in the default MatLab directory on your computer.
- Learn the basics: Proceed through the first two Matlab Getting Started tutorials that are provided when you open the software (Desktop Basics and Matrices and Arrays).
- Complete the Pre-Lab quiz on Canvas.
- Bring your computer, with MatLab installed, to the lab meeting.
- This ession is a "Dry Lab": We will meet in a classroom, thus lab attire is not necessary for this session.

*It is recommended that you install MatLab on your own computer, but there are other way to access MatLab if necessary (get access).

Be sure you complete the assignment above, including the online quiz on Canvas, before the deadline!

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14.1.3.2: MATLAB PRACTICE (IN CLASS ACTIVITY)

Note

Before attempting these exercises, please make sure you have access to a working copy of the MatLab software and you have the custom scripts and binary files installed in the MatLab directory. If you are using FastX to access MatLab on campus, these files are already installed for you on the server. Otherwise, you should install MatLab and the custom files on your computer before proceeding.

The practice exercises in this module are meant to be completed during the scheduled meeting. The Matlab practice exercises are are designed to help you become literate in MatLab programing language and the MatLab GUI's so that you can accomplish the data analysis in this course. MatLab is the preferred tool for data analysis for the modules later in this lab semester.

Both of the activities below can be completed during the first laboratory meeting; collaboration among students is welcome, though each of you should complete the activity and submit your own work. Your work should be inspected by your teaching assistant (TA) before you submit the assignments and leave for the day. If your TA determines that you have done the activities correctly, you will receive full credit for this assignment.

14.1.3.2.1: The Basics

14.1.3.2.2: Practice with LiveScript

14.1.3.2.3: MatLab for Data Analysis In This Course

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14.1.3.2.1: The Basics

Originally Created by Lindsay Pederson, Fall 2022 | Modified by Kathryn Haas each semester since.

Caution

This exercise may be an uncomfortable experience if you haven't completed the basic MATLAB tutorials that were part of your pre-lab assignment. If you are feeling lost during this activity, please go back to the basic MATLAB tutorials to get comfortable with the basic commands and practice working with matrices before returing to this exercise.

MatLab General Layout

Open the MatLab program to begin. If the layout of your MatLab window looks different than the arrangement illustrated below, you can switch to the default layout using the "Layout" button in the Home Tab toolbar (see below). Choose "Default Layout" from the "Layout" drop down menu. If the layout still seems different than what is shown it might be because you have a Script or LiveScript file open in your MatLab program.

Compare your MatLab window to what is shown below. Read the figure below and familiarize yourself with the panels of the MatLab window. Then follow the instructions.

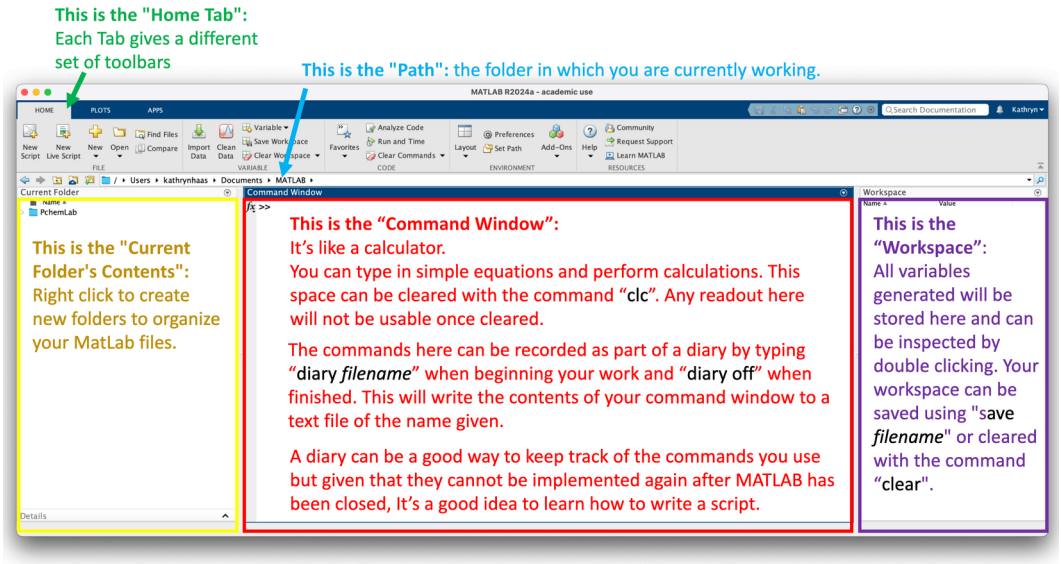


Figure 14.1.3.2.1.1: The default layout of the MatLab window (as of version R2024a). The tabs above the top toolar give access to different toolbar options. The file path is shown under the top toolar and indicates the current working folder. The Current folder's contents is shown in the pannel on the left. The center window is the Command Window, which functions like a calcuator. Type commands into the command window, save the work in the command window using the "diary filename" command to start saving and "diary off" when finished. All variables enterend in the Command Window will be populated in the Workspace, shown in the panel on the right. The Workspace can be saved using the "save filename" command or by using the "save workspace" button in the Home Tab toolbar. The workspace can be cleared using the "clear" command. (CC-NC-BY-SA; Kathryn Haas)

Practice with the Command Window

Find the command window in MATLAB. The command window is like a calculator. You can type simple equations here to perform calculations. The command window can be cleared by the command:

```
clc
```

All work is lost after the space is cleared.

The commands entered in the command window can be recorded in a text file (a diary). To record a diary, use the command "diary filename" at the beginning of your work:

```
diary filename
```

And then then at the end of the work:

```
diary off
```

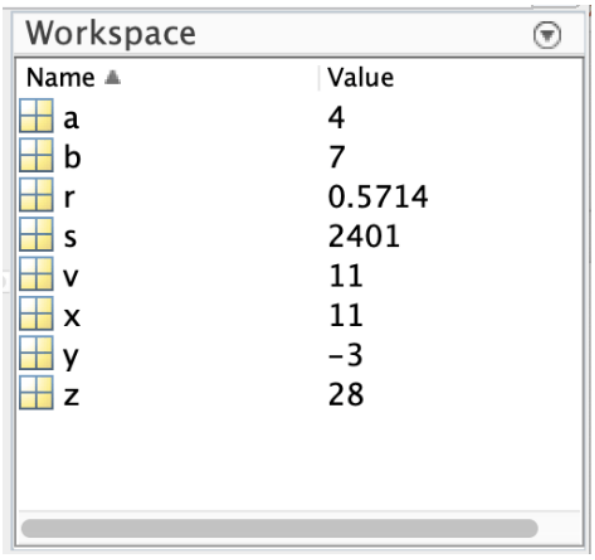
The diary file is a good way to keep track of commands, but the work cannot be implemented again from the diary file, so it has limited utility. **Script** and **Live Script** files are a much more useful way to record your work. **First, let's practice using the command window:**

Using the command window, begin a diary file with the name "practice_diary". Then do the following:

1. Clear the workspace by typing the clear command.
2. Create a variable *b* and set it equal to 7
3. Create a variable *a* and set it equal to 4
4. Add *a* and *b* and assign the result as *x*
5. Subtract *a* and *b* and assign the result as y
6. Multiply *a* and *b* and assign the result as *z*
7. Divide *a* by *b* and assign the result as r
8. Find *b* to the power of *a* and assign the result as s
9. Use the up arrow key to go back to the the command from step 4. Edit the command to assign it as *v* istead of *x* and end the command a semicolon; What does the semicolon do?
10. End the diary
11. Clear the command window with clc

The workspace

Notice that your workspace now contains all variables you defined. The workspace should look like this:



You can save the variables in the workspace as a binary ".mat file" with the command:

```
save filename
```

Use the command window to save your workspace using the file name "practice_workspace.mat". Notice the new file shows up in

the **Current Folder Window**.

Now, clear the workspace with the clear command.

```
clear
```

Just for practice, use the load command to load the file you just saved and inspect the workspace:

```
load filename
```

Clear the workspace again before moving to the next section.

Discussion Questions 14.1.3.2.1.1

1. Where was the practice_diary file saved and what extension does it have? How would you submit a file like this to Gradescope?
2. When mathematical operations are performed in the command window, how are they defined in the workspace? What happens to the previous value in the workspace when you enter a new operation? (eq, try a + b , then a^b)
3. What does a semicolon at the end of a command do?
4. What does a percentage sign at the beginning of a line do?

Practice with Script Files

The Command Window is convenient for quick operations that you don't want to save. But it has some big limitations. For example, even if you do save the diary, you can't re-run any of the commands automatically. A better way to save your work is by entering it in a Script File.

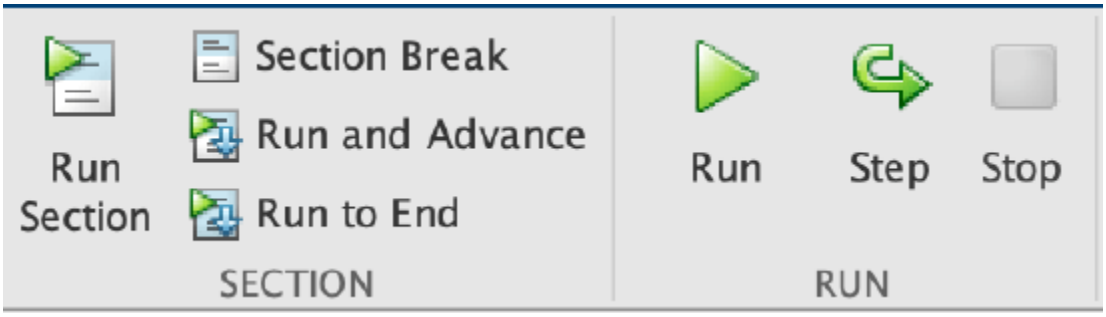
One way to start a new script is to go to the Home Tab and select **New**, then **Script**. Instead, let's use the command line to start a new script called "reference_script.m". Type the following into the command window:

```
edit reference_script.m
```

This will create a new script file. The new file should appear in the Current Folder window and it will open as a new tab in the Editor Window.

Find the Editor Window. In the Editor window, type the following:

```
%% Editor Exercises %%
% single percent sign indicates a text line
% double %% percent (only) indicates a section break.
% you can run each section of the editor by pressing the Run Section button.
% you can run the entire editor by pressing the Run button
```



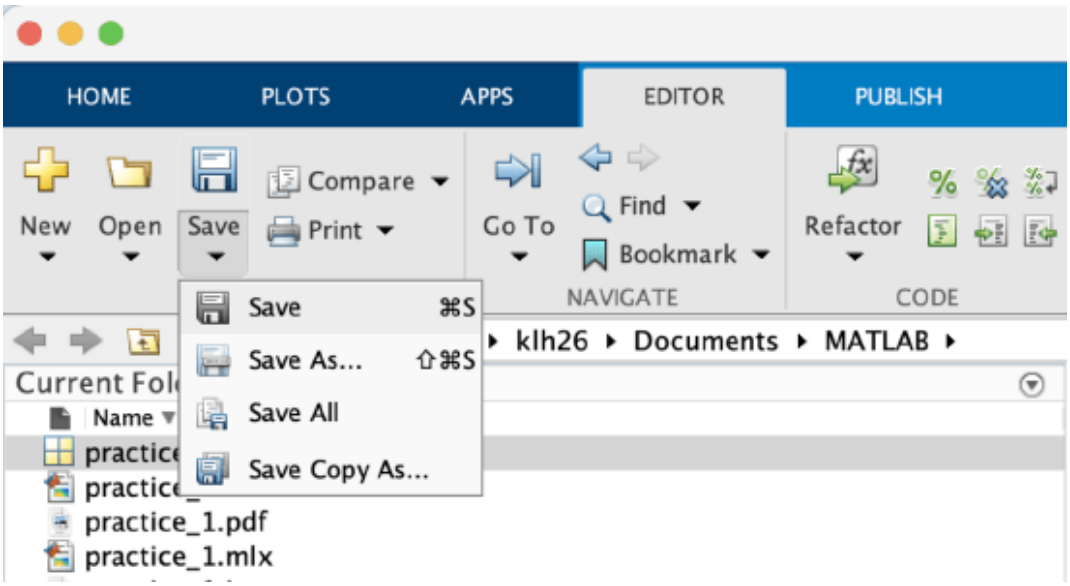

```
%%
%Type this into the new script in the Editor
b = 7
a = 4
```

```
% then hit run.
```

Notice what happens in the command window and in the workspace.

```
% again, type these examples of simple operations into the editor
x = a+b
y = a-b
z = a*b
r = a/b
s = b^a
% hit run and look at the command window
% then clear the command window and clear the workspace
% then add semicolons to the end of the lines and hit run again
```

Now that we see how the editor works, let's save the contents of the editor window as "reference_script.m". Go to the Editor tab and choose save.



At the end of the script that you just saved, add the following. Then run each section to see what happens. You can view any variables by typing their name in the command window.

```
%%
%% Building a reference sheet %%
a = 7;
b = 4;

%%
%Simple matrix - you can use spaces or commas to separate entries%
l = [1 2 3];
%%
%multiple rows - separated by semicolons%
m = [1;2;3];
%%
%matrices can have expressions in them%
n = [a+b, a-b, a*b];
%%
%transpose matrices with an apostrophe%
N = n';
%%
%multiply matrices
L = l*m;
M = m.*N;
```

```
%works the same with division
%%
%Create a matrix with regularly spaced intervals - defaults to one if not
%otherwise specified%
e = [1:16];
E = [1:0.5:16];
%%
%To reference specific elements of a matrix, call the matrix and then add
%coordinates (row, column) or just one number if it's a vector%
e7 = e(7);
m2 = m(2);
%%
%delete specific elements of a matrix
h = [1 2 3;4 5 6;7 8 9];
h(2) = [];
%check value of h in workspace
%%
%How to plot stuff
%you can just say "plot" but to intentionally keep track of figures it's a
%good idea to invoke figures by number
x = [1 2 3 4 5];
y = x.^2;
z = y./2;
figure(1)
hold on
plot(x,y)
plot(x,z,"o")
hold off
A = [1, 5, 0, 20];
axis(A)
xlabel('x')
ylabel('x^2')
title('Example')
%you can get help for any function you want to use (ex: plot()) by searching
%in the "Search Documentation" box at the top right of the screen
```

Save your files. Then clear the workspace and command windows before proceeding to the next section.

Discussion Questions14.1.3.2.1.2

1. What is the purpose of the period in the following statement? What happens if the period is removed?

   ```
   M = m.*N;
   ```

2. How can you delete the value 0.4 in the following matrix?

   ```
   mat1 = [0.1 0.2 0.3 0.4 0.5 0.9 1.0];
   ```

3. What does the "o" specification do in the code below:

   ```
   plot(x,z,"o")
   ```

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14.1.3.2.2: Practice with LiveScript

Install a custom script

The custom scripts (files with .m extension) and binary files (files with .mat extension) for this course are available here (click to go to GoogleDrive) using your Google account. If you are using the Chemistry Department *bohr* server to access Matlab, the scripts are already installed for you.

If you are using your own computer, the scripts and binary files should be added to the correct folder on your computer. Follow the instructions in this video to install the lsq script, which performs least squares analysis.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Practice using a custom script and a binary file

This is an exercise to give you some practice in using Matlab to analyze data provided in a binary file, and plot the results using a custom script for least squares analysis. Before you start, make sure the custom files lsq.m and expt-1.mat are in your working MatLab directory (see video above). The binary file "expt-1" simply contains pre-defined 80 x 1 vector matrixes "x" and "y". This is just to save you the hassle of typing in the values for each vector.

> Open the "Practice_LiveScript_XXX.mlx" file, and simply follow the instructions within the Live Script document.

The file linked above will walk you through the following steps to create a "final" plot.

1. Open the MatLab program and be sure that you are working in the directory containing the lsq script and expt-1 binary file.
2. Type the following: **load expt-1**
   Your workspace now contains two variables, x and y which obey the following relation:
$$y = Ae^{-Cx} \tag{14.1.3.2.2.1}$$
3. Plot y (ordinate) versus x (abscissa). Using Matlab, recalculate your data in linear form (ln y versus x) and plot the result. Using least squares analysis of the linearized data, calculate the values of A and C and report the standard deviation in these values. Using your calculated values of A and C, use Matlab to draw (a) the least-squares fitted line through your linear plot and (b) the best fit curve through your exponential plot. (NOTE: data should appear as points using the symbol 'o' and least squares fitted lines should be solid lines.)

   > **Expectation for a "final" full-credit plot in this course:**
   >
   > - Data is plotted in scatter format.
   > - Axes are correctly labeled, with correct units.
   > - When appropriate, a curve fit to the data is shown
   >   - equation of the line is shown on the plot, but not obscuring the data
   >   - uncertainty in slope and intercept provided

    - correlation coefficient (R) provided
  - Approrpate units are given for every value and every axis label.
  - Plot is centered on graph.
  - Text is easily readable (usually this means it is large enough to read easily.

4. You should show the plots described in (3) together with the values of A and C to your instructor. Each graph should have a title, and the x- and y-axes should be labeled.

This is an old video of this activity (before LiveScript files were developed.)

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

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14.1.3.2.3: MatLab for Data Analysis In This Course

MatLab is the preferred tool for data analysis in this course. That means that we will provide MatLab templates for your data analysis in each module and we can provide some basic support for your computational work if you use MatLab. However, if you have a favorite tool that is not MatLab, you are welcome to use it instead from now on, but please know that your instructional team may not be able to offer technical support for other computational programs.

We provide the MatLab Live Script files that can support your work in the modules this semester. Let's take a close look at the one for your "Error Analysis" problem set (your next assignment, in Module 3).

With any time remaining in the class meeting, or with your time out of class, access the MatLab files for this course and find the "Treatment of Error folder". From this folder, open the file called "Error_StudentGuide_date.mlx" and follow the instructions within to begin completing your next assignment. Also proceed to the next module (Module 3) in this manual to view the pre-lab assignment for your next meeting.

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14.1.3.3: HOW TO ACCESS MATLAB (DUKE STUDENTS)

15.3: How to Access MatLab (Duke students)

14.1.3.3.1: Install Matlab on your own computer

14.1.3.3.2: Access MatLab Remotely Through FastX

14.1.3.3.2.1: Transferring Files Between Your Computer and Your Duke NetID Account

14.1.3.3.2.2: Access from off-campus (The Duke VPN)

14.1.3.3.3: Invoking Matlab From the Lab Computers

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14.1.3.3.1: Install Matlab on your own computer

Another way access MatLab is to download and install the software on your own computer. The MatLab software with the additional "toolboxes" will take approximately 4 GB of space on your computer. If you have enough space on your computer to operate this software you can find instructions for downloading and installing the software at the links below.

- Duke OIT's Software List: https://software.duke.edu/
- Duke MatLab Portal: https://www.mathworks.com/academia/tah-portal/duke-university-30359028.html

If the links above are not working, try to search "Duke MatLab" on an internet browser and you will find the most recent information. (And please inform your instructors of any dysfunctional links!)

Additional Installation Instructions

During the installation of the software, it will be most convenient if you select to also install the following toolboxes in the PRODUCTS screen of the MatLab Installer (See image below).

- Curve Fitting
- Statistics and Machine Learning
- Symbolic Math

If you forget to do this, it can be done later through the Apps Tab in MatLab.

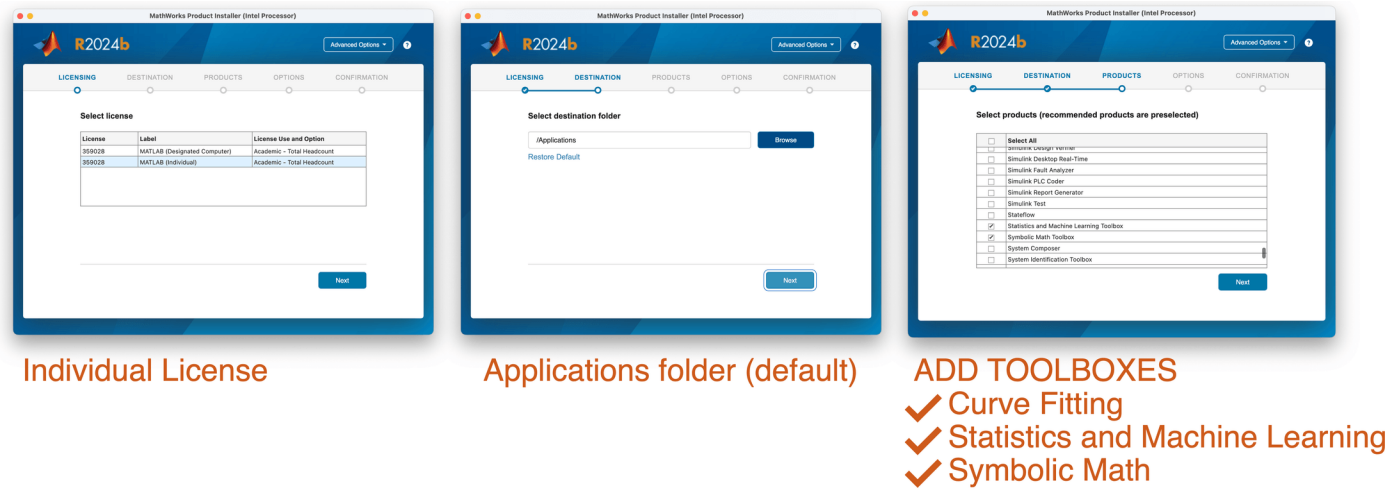


Figure 14.1.3.3.1.1: MatLab Install options. (Kathryn Haas; CC-NC-BY-SA)

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14.1.3.3.2: ACCESS MATLAB REMOTELY THROUGH FASTX

Use FastX to Access Software

This document describes two ways to access the server versions of Matlab, and later in the semester Spartan, from your own computer. These programs are housed on a chemistry server called bohr (at bohr.chem.duke.edu). You can access this server either by downloading and installing FastX; or, you can access bohr directly from your web browser. Both options are described below

Option 1: Download and Install FastX on Your Computer:

1. Copies of both the Windows and Macintosh Installers are available from the Software section of the OIT web site, www.oit.duke.edu/software. Download and install the appropriate one for your computer. Installation is quick and straightforward, just follow the prompts.



2. Once installed, Launch the program from the icon.

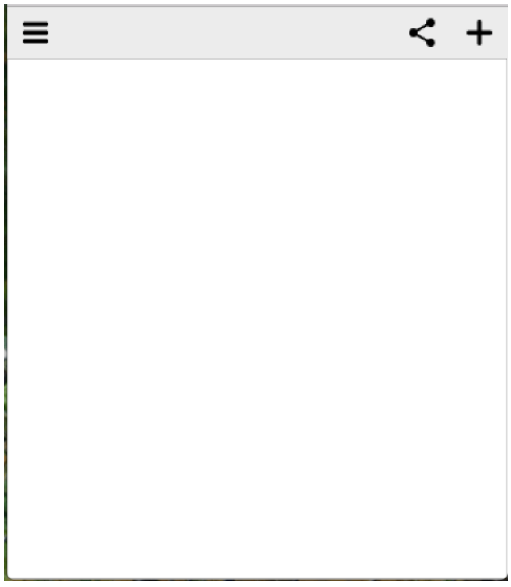


Figure 14.1.3.3.2.1: Configuring FastX. (CC-NC-BY-DUKE CHEM)

3. Click on the + sign at the upper right of the main window. Select SSH from the menu that appears.
4. Complete the New SSH connection box as follows:

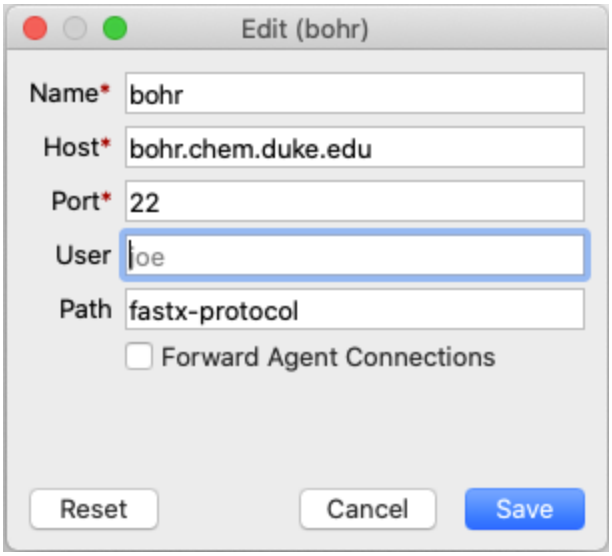


Figure 14.1.3.3.2.2: bohr.chem.duke.edu. (CC-NC-BY-DUKE CHEM)

For Name, call it Bohr, or really anything you want. For Host, enter bohr.chem.duke.edu. The Port should be 22. Enter your NetID username in the User box. The Path box should already be correct. Click on the Save button when done. The program will attempt to connect to bohr.chem.duke.edu. If you get a message saying the system is not recognized by this computer (or something to that effect), click Continue. When prompted, enter your NetID (if you didn't add it to the connections setup box) and password.

5. Click on one of the xterm choices from the new window that appears.



Figure 14.1.3.3.2.3: Choose xterm. (CC-NC-BY-DUKE CHEM)

6. An x-terminal window will open. At the prompt type,

```
matlab
```

Option 2: Use FastX directly from a web browser:

1. Open a browser. We suggest using Chrome or Firefox, but likely any browser will work.
2. Navigate to https://bohr.chem.duke.edu:3300

When Prompted enter your NetID Username and Password

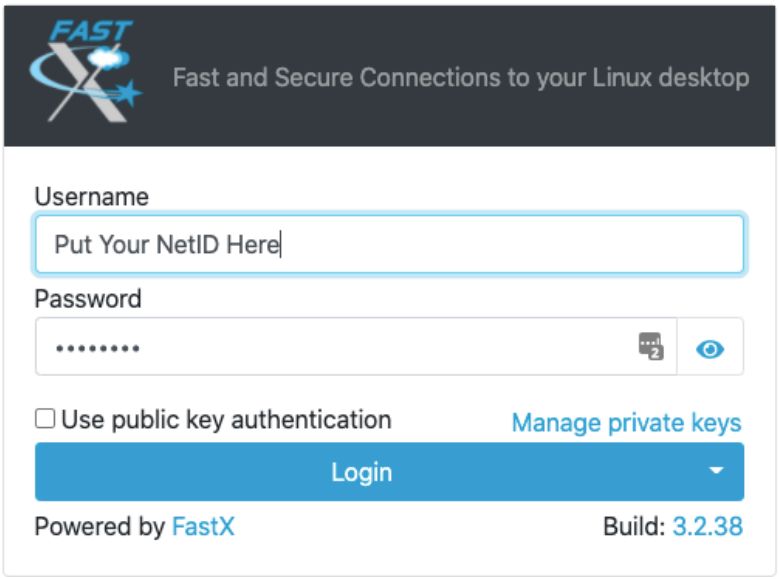


Figure 14.1.3.3.2.4: FastX Login From Web Browser. (CC-NC-BY-DUKE CHEM)

3. Click on the blue + at the top left of the next screen.

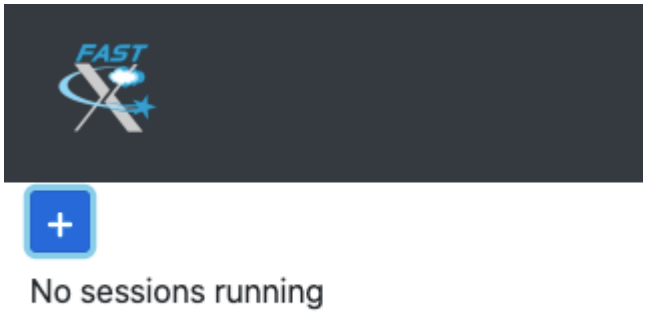


Figure 14.1.3.3.2.5: The New Session Button. (CC-NC-BY-DUKE CHEM)

4. Select xterm from the options on the next screen. Click Launch to start the session.

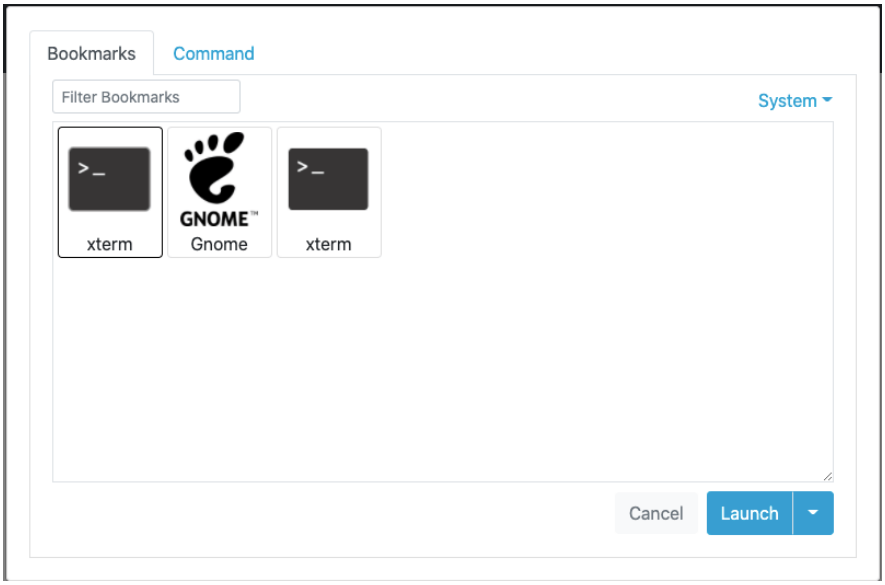


Figure 14.1.3.3.2.6: Launch a new Xterm Session. (CC-NC-BY-DUKE CHEM)

When your xterminal window appears, type,

```
matlab
```

at the prompt.

14.1.3.3.2.1: Transferring Files Between Your Computer and Your Duke NetID Account

14.1.3.3.2.2: Access from off-campus (The Duke VPN)

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14.1.3.3.2.1: Transferring Files Between Your Computer and Your Duke NetID Account

In several experiments this semester, you will use a lab computer for instrument control and data acquisition. There are times when it is convenient to have your raw data files uploaded to bohr so that you might analyze the data using Matlab. Additionally, there are times when files and figures (graphs) that are generated by matlab need to downloaded to your own computer. These operations can be done in the following manner.

1. To upload files from one of the lab computers to your online account:

1.1. Click on the 

icon found on the computer desktop to start the WinSCP file transfer program. The File protocol should be SFTP, and the port should be 22. Enter login.oit.duke.edu under Host Name. Enter your NetID (User name) and password, and click on Login. Click Continue at the Authentication Banner.

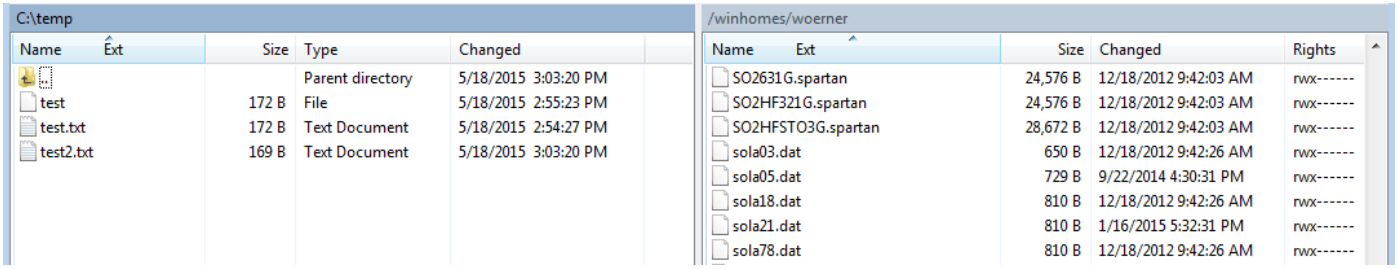
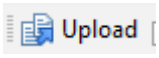


Figure 14.1.3.3.2.1.1: The Main WinSCP Window. (CC-NC-BY-DUKE CHEM)

1.2. You will see a dialog box, part of which is shown above. On the left-hand side of the screen is your local directory (i.e., the directory of the lab computer). It should default to the directory containing your data. If not, change the directory to the correct one. You should see a list of those files found in the local directory. On the right-hand side you will see the contents of your OIT account.

1.3. To transfer files from the local PC to your OIT account, first highlight the appropriate files you want transferred. Click on the 

button at the top of the screen. An Upload dialog box will appear. Click OK to copy your files from the local PC to your OIT account. Or, click on Transfer Settings if you want to check to see that the transfer is configured properly. (In general, the Transfer mode should be Text and the File modification should be No change.) Then click on **Copy**. Check to be sure all of your files are transferred and then exit your session by clicking the X at the upper right corner of the screen.

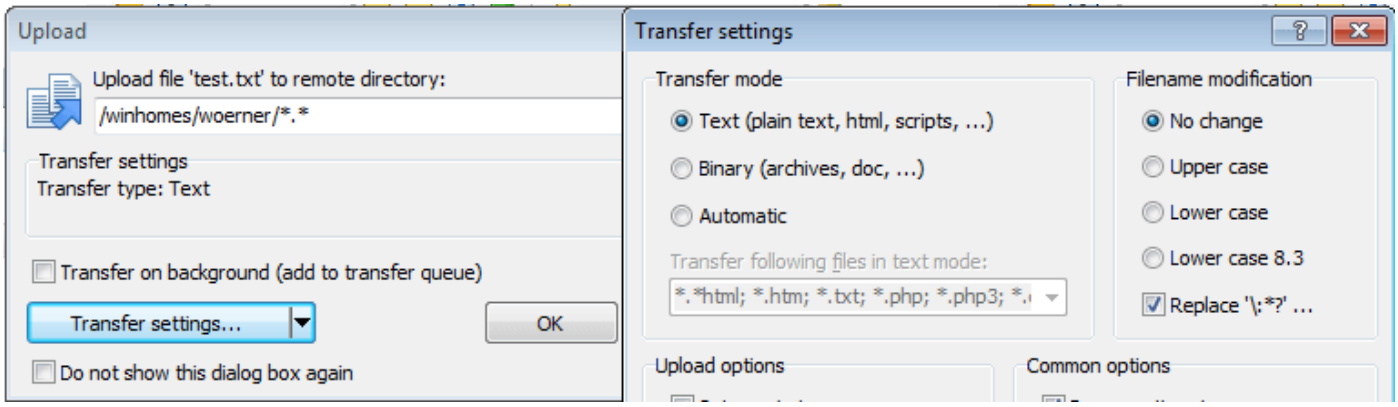


Figure 14.1.3.3.2.1.2: The WinSCP Upload Screen. (CC-NC-BY-DUKE CHEM)

2. **Downloading** files from your OIT account to your own **Windows** computer or to one of the lab computers is accomplished in the same manner, except that you should select the files you want to download, and execute the transfer from your OIT account to your local computer.

3. **Transferring** files back and forth between your **Macintosh** computer and your OIT account can be accomplished in the following manner.

3.1. From the Go menu (found when you are in your Finder), select **Connect to Server**.



Figure 14.1.3.3.2.1.3: The Macintosh Go Menu. (CC-NC-BY-DUKE CHEM)

3.2. In the text box at the next screen enter,

`smb://homedir.win.duke.edu/users/the first letter of your NetID/your full NetID`

An example of a correct server address is shown below, where w is the first letter of the NetID, and woerner is the NetID.

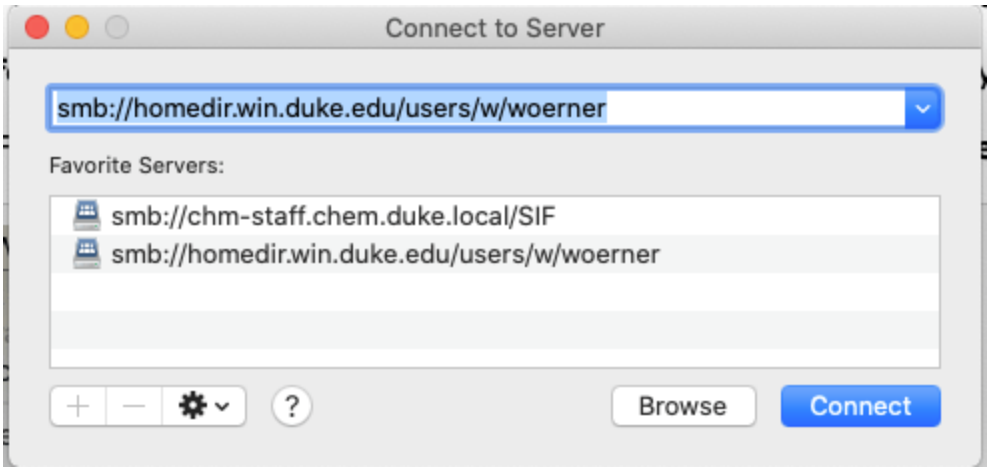


Figure 14.1.3.3.2.1.4: The Connect to Server Screen. (CC-NC-BY-DUKE CHEM)

3.3. Click the **Connect** button. You will be prompted for your NetID and Password.

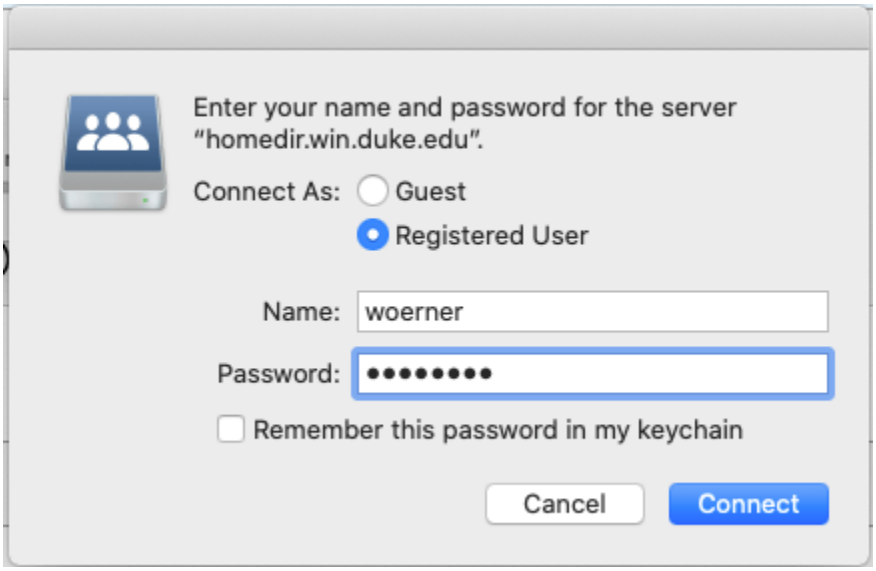


Figure 14.1.3.3.2.1.5: Login Screen. (CC-NC-BY-DUKE CHEM)

3.4. Once connected a new icon will appear on your desktop.



Figure 14.1.3.3.2.1.6: The Connectred Server Icon. (CC-NC-BY-DUKE CHEM)

If you do not see the icon appear, Check the **Finder Preferences**,

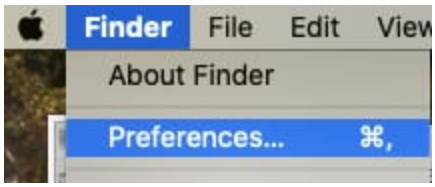


Figure 14.1.3.3.2.1.7: The Finder Menu. (CC-NC-BY-DUKE CHEM)

and make sure Connected Servers is checked.

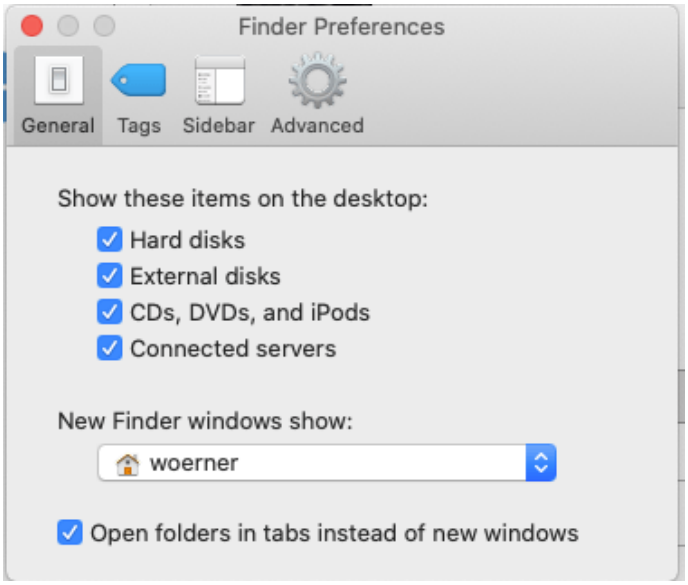


Figure 14.1.3.3.2.1.8: Finder Preferences. (CC-NC-BY-DUKE CHEM)

3.5. The connected server on your desktop acts like any other folder on your Mac. Click on it to open it and see the contents of your online OIT account. Drag and drop to move files back and forth between your Mac and your OIT account.

This page titled 14.1.3.3.2.1: Transferring Files Between Your Computer and Your Duke NetID Account is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

14.1.3.3.2.2: Access from off-campus (The Duke VPN)

If you are planning to access Matlab, or later in the semester Spartan, from an off-campus location you will need to install and run the Duke **V**irtual **P**rivate **N**etwork (VPN) software. Complete instructions for downloading, installing, and running the Duke VPN software can be found here:

For Windows computers.

For Macintosh computers.

Remember to start the VPN before accessing Matlab (or Spartan) from an off-campus location.

This page titled 14.1.3.3.2.2: Access from off-campus (The Duke VPN) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

14.1.3.3.3: Invoking Matlab From the Lab Computers

INVOKING MATLAB FROM COMPUTERS IN THE LABS

1. To start Matlab on any of the computers in the lab:



FastX

1. Click on the FastX icon, on the main desktop screen, and then on the bohr.chem.duke.edu session. Enter your NetID and password and click OK. Once logged in, click on the + in the upper right of the bohr.chem.duke.edu window.

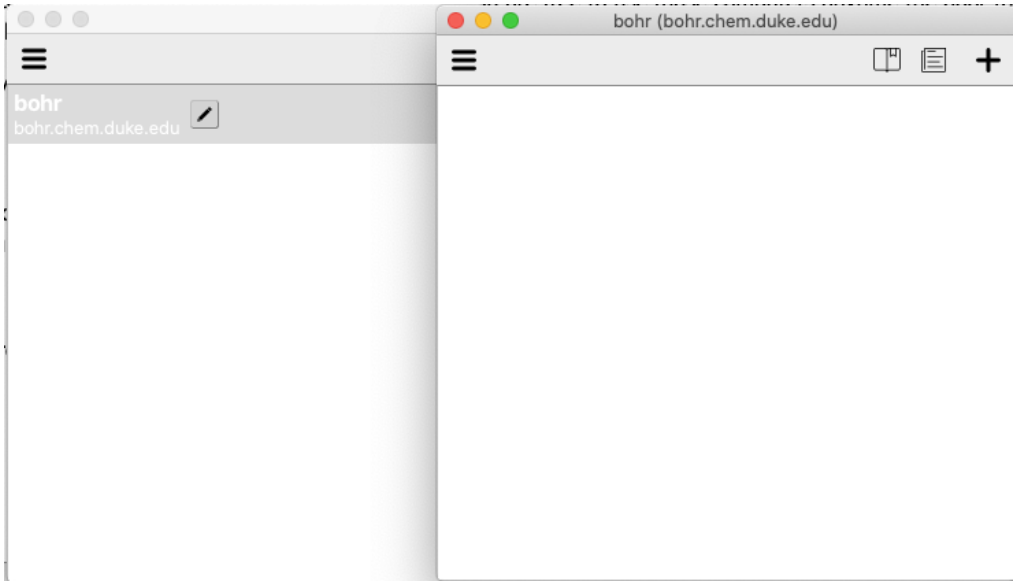


Figure 14.1.3.3.3.1: Connecting to Bohr through FastX. (CC-NC-BY-DUKE CHEM)

2. Click on one of the xterm choices from the new window that appears.



Figure 14.1.3.3.3.1: Choose xterm. (CC-NC-BY-DUKE CHEM)

3. An x-terminal window will open. At the prompt type,

```
matlab
```

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14.1.3.4: USING MATLAB (SUPPLEMENTAL)

> If you are a brand new Matlab user, or its been a long time since you've used it, the "hopw-to" sections of this manual may seem opaque. A great way to start it to run through the "Getting Started" tutorials from Matlab.

We will introduce you to using Matlab to perform numeric calculations. If you wish, you may save a copy of your work for printing later. This is done using the **diary** command, which captures a copy of all subsequent keyboard input and most of the resulting output (with the exception of graphs) to be written to a named file. If the file already exists, the output is appended to the end of the file. For example, the command,

```
diary exptA
```

will save your work in the file exptA. This file can be downloaded to your computer for later use as described in section 1.2.15. When you have completed your work, the command,

```
diary off
```

will suspend the diary.

> **IMPORTANT NOTE:**
>
> The diary command merely "records" your on-screen work. It does not save your data. Data must be saved as described in Section 1.2.12. Although diary files may be printed, they cannot be retrieved for viewing on the screen.

14.1.3.4.1: Linear Least Squares Analysis

14.1.3.4.2: Last Line Editing and Recall

14.1.3.4.3: Saving Data

14.1.3.4.4: Deleting Matrices

14.1.3.4.5: Quitting Matlab

14.1.3.4.6: Entering Matricies

14.1.3.4.7: Matrix Computation

14.1.3.4.8: Vectors

14.1.3.4.9: Subscripting

14.1.3.4.10: Finding, Deleting, Adding or Replacing Data

14.1.3.4.11: Output Format

14.1.3.4.12: The Help Facility

14.1.3.4.13: Array Operations

14.1.3.4.13.1: Array Addition and Subtraction

14.1.3.4.13.2: Array Multiplication and Division

14.1.3.4.13.3: Array Powers

14.1.3.4.13.4: Math Functions

14.1.3.4.14: Graphics

14.1.3.4.14.1: Basic Plots

14.1.3.4.14.2: Line Types
14.1.3.4.14.3: Multiple Plots
14.1.3.4.14.4: Manual Axis Scaling
14.1.3.4.14.5: Overlaying Plots

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14.1.3.4.1: Linear Least Squares Analysis

To fit a straight line, y = mx + b, to a set of experimentally determined points

(x 1,y 1), (x 2,y 2), ..., (x n,y n) contained in the vectors [x] and [y], use **Basic Fitting** under the **Tools** menu in your graph window. Try this using the following data:

```
x = [-3.8 -1.2 0.75 3.1 5.6 8];
y = [8.2 6 3.3 1.6 -2 -6];
```

Selecting Basic Fitting from the Tools menu opens up an options box. Select **linear** as the fit type and choose how many significant figure you want in the calculation. A Linear Least-Squares line will be placed on the graph along with the equation for the line.

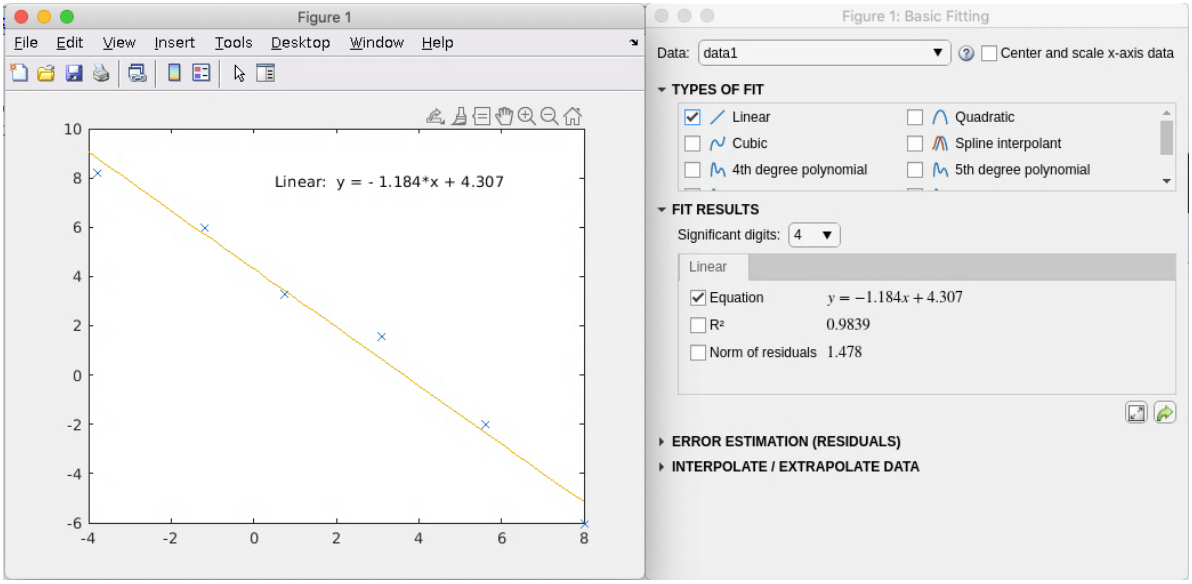


Figure 14.1.3.4.1.1: Basic Linear Fit. (CC-NC-BY-DUKE CHEM)

NOTE: Often for our purposes in the Physical Chemistry Laboratory it is often important to know the uncertainties (or standard deviation) in the calculated slope and intercept. To obtain calculated values of the slope, intercept, correlation coefficient along with the uncertainties in slope and intercept, use the **lsq** command. Using the current x,y data as an example, typing:

```
lsq(x,y)
```

returns the following:

```
>> x=[-3.8 -1.2 .75 3.1 5.6 8];
>> y=[8.2 6 3.3 1.6 -2 -6];
>> plot(x,y)
>> lsq(x,y)
        **********************************************************************
                Slope =  -1.1839
                Y Intercept =   4.3066
                Standard Deviation of Slope = 0.075611
                Standard Deviation of Y-Intercept =  0.34013
                Correlation Coefficient = -0.9919

                Standard Error of Estimate =   0.7392
                (measure of y-scatter about regression line)


                WRITE THESE RESULTS IN YOUR LAB NOTEBOOK !
        **********************************************************************
```

Figure 14.1.3.4.1.2: The lsq Function. (CC-NC-BY-DUKE CHEM)

To perform a weighted linear least-squares analysis, you would use the command **wtlsq(x,y)**. This requires that you enter a weighting factor e.

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14.1.3.4.2: Last Line Editing and Recall

The arrow keys on the terminal can be used to edit mistyped commands or to recall previous command lines. For example, suppose you enter

```
log(sqt(atan(2*(3+4))))
```

You have misspelled sqrt. The response from Matlab is the error message,

Undefined function ‘sqt’ for input arguments of type 'double'.

Instead of retyping the entire line, simply hit the Up-Arrow key. The incorrect line will be displayed again and you can move the cursor over using the Left-Arrow key and insert the missing r.

```
log(sqrt(atan(2*(3+4))))
```

ans = 0.2026

The arrow keys on the keyboard work on copies of the previous input lines, which have been saved in a moderately sized input buffer. Here is a brief description of their function:

Last-line Editing and Recall Keys

Up Arrow Recalls previous lines.

Left Arrow Move left one character.

Right Arrow Move right one character.

Ctrl-U Cancel current line.

Ctrl-E Move to end of line.

Ctrl-A Toggle between insert and overtype mode.

Delete Delete character at cursor.

Backspace Delete character left of cursor.

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14.1.3.4.3: Saving Data

If you wish to save the variables in your workspace for later use, enter:

```
save filename
```

This saves all variables in the file *filename.mat*.. The next time you invoke Matlab, the workspace may be restored using:

```
load filename
```

We highly recommend that you save your data frequently as you work. This will prevent a major loss of data in the event of a system failure.

If you wish to save graphics, work from within the graphics window. Choose **Save** from the **File** menu. A dialog box opens up. Give your file a name, in the **File Name** box. You can select the file type from the **Files of Type** menu. Matlab graphics default to a .fig file type, and if you intend to open the graph again in Matlab that is a good option. If you want a picture of the graph for use in electronic lab notebooks (ELN's) or in your formal written reports you might prefer the .jpg format. The file will be stored in the specified directory (shown in the Save In menu) of your account associated with your NetID when you click on the **Save** button.

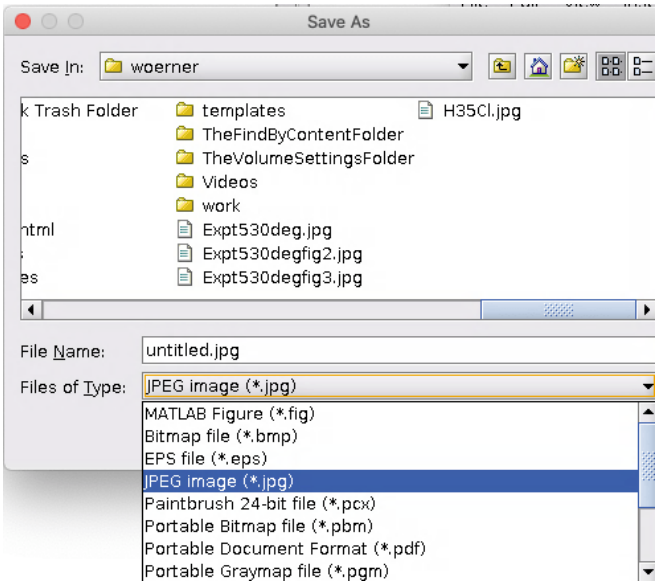


Figure 14.1.3.4.3.1: Saving a Figure.

Saved .fig files can be opened anytime, from the Matlab prompt, by typing

```
open filename.fig
```

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14.1.3.4.4: Deleting Matrices

If you wish to delete a variable from your workspace, enter:

```
clear name
```

where *name* is the name of the matrix or variable to be deleted.

> **Note**
>
> Be careful, because executing,
>
> **clear**
>
> by itself, clears **all** variables from the workspace!

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14.1.3.4.5: Quitting Matlab

Before you exit Matlab type,

```
diary off
```

if you had a diary running.

Exit Matlab by typing,

```
exit
```

Type,

```
exit
```

to close any xterm windows you have open. Finally, please remember to exit out of FastX if you are accessing Matlab through a FastX connection.

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14.1.3.4.6: Entering Matricies

Matlab works with essentially only one kind of object, a rectangular numerical matrix. In some situations, special meaning is attached to 1-by-1 matrices, which are scalars, and to matrices with only one row or column, which are vectors.

Matrices can be introduced into Matlab in several different ways. The easiest method for small matrices is to use an explicit list. The explicit list is surrounded by square brackets, and uses the semicolon, ; , to indicate the ends of the rows. For example, to enter a 3-by-3 matrix, we type:

```
A = [1 2 3; 4 5 6; 7 8 0]
```

This results in the output

A =

1 2 3
4 5 6
7 8 0

The matrix A is saved for later use. The individual elements in the input should be separated by commas or blanks and can be any Matlab expression. For example, typing

```
x = [-1.3, 4/5, 4*atan(1)]
```

uses Matlab like a calculator and results in

x =

-1.3000 0.8000 3.1416

Matrices entered, horizontally, as shown above, can sometimes be long enough to require more than one line. Matlab must be told when a wrap to another line is wanted. To do this, as you near the end of the line, add a space (spacebar) followed by three periods (...). Then hit enter. You will be allowed to continue entering numbers into the same matrix on the new line. Alternatively, if entering matrices horizontally is troublesome, you can always enter numbers vertically.

Typing:

```
y = [1
2
3
4
5]
```

results in:

y=

1

2

3

4

5

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14.1.3.4.7: Matrix Computation

We will run through some basic matrix operations. Operations and commands in Matlab are intended to be natural, in a matrix sense, not unlike how they might be indicated on paper. For example, our matrix A can be transposed with:

```
B = A'
```

which results in:

```
B =

1 4 7
2 5 8
3 6 0
```

Transposing x,

```
x = x'
```

results in:

```
x =

-1.3000
0.8000
3.1416
```

Matrix multiplication is indicated with:

```
C = A * B
```

producing:

```
C =

14 32 23
32 77 68
23 68 113
```

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14.1.3.4.8: Vectors

Vectors with regularly spaced elements may be generated using the colon:operator.

The statement

```
D = 1:4
```

results in

D =

1 2 3 4

Two colons may be used to create vectors with increments between the elements. Typing:

```
E = 0:0.1:0.5
```

results in

E =

0.0000 0.1000 0.2000 0.3000 0.4000 0.5000

Vectors are used often in Matlab because of the ease with which they allow data manipulation and function evaluation. When a function is applied to a vector in Matlab, the function is applied to each element of the vector. For example, consider taking the sine of the four elements in vector D above. Typing:

```
Y = sin(D)
```

results in

Y =

0.8415 0.9093 0.1411 –0.7568

A wide variety of data analysis functions are available that operate on vectors. Typical functions include cumulative sum,

```
cumsum(Y)
```

ans =

0.8415 1.7508 1.8919 1.1351

mean and standard deviation,

```
m = mean(Y), s = std(Y)
```

m =

0.2838

s =

0.7758

Other useful functions include:

max(x)	returns the largest element in the vector x
min(x)	returns the smallest element in the vector x
median(x)	returns the median value of the vector x
sort(x)	sorts the elements of x in ascending order
sum(x)	returns the sum of the elements of x

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14.1.3.4.9: Subscripting

Enclosing their subscripts in parentheses may reference individual matrix elements. The statement A(m,n) refers to the mth row, and nth column, of matrix A. For example, given a matrix A:

```
A =

1 2 3
4 5 6
7 8 9
```

the statement

```
A(3,3) = A(1,3) + A(2,2)
```

results in

```
A =

1 2 3
4 5 6
7 8 8
```

A subscript can be a vector. If X and V are vectors, then X(V) is [X(V(1)), X(V(2)), ..., X(V(n))]. For matrices, vector subscripts allow access to contiguous and noncontiguous submatrices. For example, suppose that A is a 10-by-10 matrix. Then,

```
A(1:5,3)
```

specifies the 5-by-1 submatrix, or column vector, that consists of the first five elements in the third column of A. Similarly,

```
A(1:5,7:10)
```

is the 5-by-4 submatrix of elements from the first five rows and the last four columns.

Using the colon by itself in place of a subscript denotes *all* of the corresponding row or column. For example,

```
A(:,3)
```

is the third column and

```
A(1:5,:)
```

is the first five rows.

In general, if v and w are vectors with integer components, then

```
A(v,w)
```

is the matrix obtained by taking the elements of A with row subscripts from v and column subscripts from w.

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14.1.3.4.10: Finding, Deleting, Adding or Replacing Data

The following examples will illustrate how to find, change, add or delete data in a vector. The same principles apply to manipulation of data in matrix form.

(a) Finding Data:

Suppose we wish to find the elements of vector V which are greater than or equal to 7:

```
V = [-2 3 7 -26 48 10 -8]', i = find(V>=7)
```

results in

V =

-2

3

7

-26

48

10

-8

i =

3

5

6

The statement, i = find(V>=7), returns a vector, i, containing the index of the elements of V which are greater than or equal to 7. The third, fifth and sixth elements of V are ≥ 7.

There are six relational operators that can be used in Matlab:

Relational Operators

< less than

<= less than or equal to

> greater than

>= greater than or equal to

== equal to

~= not equal to

(b) Deleting Data:

Specific elements in a matrix or vector can be deleted using the empty matrix (or vector), []. The statement

```
x = []
```

assigns a matrix of dimension zero-by-zero to x. To delete the elements of V which are greater than or equal to seven, use the command

```
V(i) = []
```

which returns

V =

-2

3

-26

-8

The elements of V which have indices given by the elements of i, are removed by assigning them to an empty matrix. Single elements may be removed in similar fashion. The command

```
V(3) = []
```

deletes the third element of V and returns

V =

-2

3

-8

An efficient way of removing rows and columns of a matrix is to assign them to an empty matrix. The command, **A(:,3)=[],** deletes column 3 of matrix A.

(c) Adding Data:

Suppose we wish to combine the elements of vectors V and U:

```
U = [3:2:10]', W = [V; U]
```

This returns

U =

3

5

7

9

W =

-2

3

-8

3

5

7

9

If we wish to add a single data point (-17) to the end of vector W:

```
W = [W; -17]
```

This returns

W =

-2

3

-8

3

5

7

9

-17

(d) Replacing Data:

To replace the fourth element of W with -12, enter the following

```
W(4) = -12
```

This returns

W =

-2

3

-8

-12

5

7

9

-17

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14.1.3.4.11: Output Format

The result of any Matlab assignment statement is displayed on the screen, as well as assigned to the specified variable or to **ans** if no variable name is given. The numeric display format can be controlled using the **format** command. **format** affects only how matrices are displayed, not how they are computed or saved (Matlab performs all computation in double precision).

If all the elements of a matrix are exact integers, the matrix is displayed in a format without any decimal points. For example,

```
x = [-1 0 1]
```

always results in

x =

-1 0 1

If at least one of the elements of a matrix is not an exact integer, there are several possible output formats. The default format, called the **short** format, shows approximately 5 significant decimal digits. The other formats show more significant digits or use scientific notation. As an example, suppose

```
x = [4/3 1.2345e-6]
```

The formats, and the resulting output for this vector, are:

format short

1.3333 0.0000

format short e

1.3333E+000 1.2345E-006

format long

1.33333333333333 0.00000123450000

format long e

1.333333333333333e+00 1.234500000000000e-06

For the long formats, the last significant digit may appear to be incorrect, but the output is actually an accurate decimal representation of the binary number stored in the computer.

With the short and long formats, if the largest element of a matrix is larger than 1000 or smaller than 0.001, a common scale factor is applied to the entire matrix when it is displayed. For example,

```
x = 1.e20*x
```

multiplies x by 1020 and results in the display

x =

1.0E+020 *

1.3333 0.0000

One final command, **format compact**, suppresses many of the line-feeds that appear between matrix displays and allows more information to be shown on the screen.

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14.1.3.4.12: The Help Facility

A HELP facility is available, providing online information on most Matlab topics. To get a list of HELP topics, type

```
help
```

To get HELP on a specific topic, type help **topic**. For example,

```
help eig
```

provides HELP information on the use of the eigenvalue function,

```
help []
```

tells how to use brackets to enter matrices, and

```
help help
```

is self-referential, but works just fine.

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14.1.3.4.13: ARRAY OPERATIONS

We use the term **array operations** to refer to element-by-element arithmetic operations, instead of the usual linear algebraic matrix operations denoted by the symbols * / \ ^ '. Preceding an operator with a period **.** indicates an array or element-by-element operation.

14.1.3.4.13.1: Array Addition and Subtraction

14.1.3.4.13.2: Array Multiplication and Division

14.1.3.4.13.3: Array Powers

14.1.3.4.13.4: Math Functions

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14.1.3.4.13.1: Array Addition and Subtraction

For addition and subtraction, the array operations and the matrix operations are the same, so + and - can be regarded as either matrix or array operations.

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14.1.3.4.13.2: Array Multiplication and Division

Array, or element-by-element, multiplication is denoted by **.***. If **A** and **B** have the same dimensions, then **A .* B** denotes the array whose elements are simply the products of the individual elements of **A** and **B**. For example, if

x = [1 2 3]; y = [4 5 6];

then,

```
z = x.*y
```

results in

z =

4 10 18

X = A./B is a solution to X.*B = A and X = A.\B is a solution to A.*X = B so, the expressions A./B and A.\B give the quotients of the individual elements.

```
z = x.\y
```

results in

z =

4.0000 2.5000 2.0000

To obtain the reciprocal of the elements of x, type

```
w = x.\1
```

This results in

w =

1.0000 0.5000 0.3333

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14.1.3.4.13.3: Array Powers

Element-by-element powers are denoted by **.^**. Here are several examples, using the above vectors x and y. Typing

```
z = x.^y
```

results in

z =

1 32 729

The exponent can be a scalar.

```
z = x.^2
```

z =

1 4 9

Or, the base can be a scalar.

```
z = 2 .^x
```

z =

2 4 8

Note

This last example illustrates one of Matlab's syntactic subtleties. Although it is difficult to see, the space between the digit 2 and the period **.** is important. If it were not there, the period would be interpreted as a decimal point associated with the 2. An alternative to the space is to use parentheses, forcing the correct precedence.

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14.1.3.4.13.4: Math Functions

Available math functions include the following:

MATH FUNCTIONS

Use the Help command to obtain further information on any of these functions

abs	absolute value or complex magnitude
sqrt	square root
real	real part
imag	imaginary part
round	round to nearest integer
exp	exponential base e
log	natural logarithm
log10	log base 10
sin	sine
cos	cosine
tan	tangent
asin	arcsine
acos	arccosine
atan	arctangent

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14.1.3.4.14: GRAPHICS

One of the major advantages of Matlab is its graphics capability. The graphics commands are natural and easy-to-use, yet still succinct, powerful, and extensible.

Scientific and engineering data are examined graphically in Matlab by using a "graph" command to create a plot on the screen. There are seven different types of "graph" from which to choose:

GRAPH

plot linear X-Y plot
loglog loglog X-Y plot
semilogx semi-log X-Y plot (x-axis logarithmic)
semilogy semi-log X-Y plot (y-axis logarithmic)
polar polar plot
mesh 3-dimensional mesh surface
contour contour plot

The **plot** command creates linear X-Y plots. Once the plot command is understood, logarithmic and polar plots are created by substituting the commands **loglog**, **semilogx**, **semilogy**, or **polar** for **plot**. All five commands are used the same way; they only affect how the axis is scaled and the data are displayed.

14.1.3.4.14.1: Basic Plots

14.1.3.4.14.2: Line Types

14.1.3.4.14.3: Multiple Plots

14.1.3.4.14.4: Manual Axis Scaling

14.1.3.4.14.5: Overlaying Plots

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14.1.3.4.14.1: Basic Plots

If Y is a vector, plot(Y) produces a linear plot of the elements of Y versus the index of the elements of Y. For example, suppose we would like to plot the numbers {0., .48, .84, 1., .91, .6, .14}. This is quickly accomplished by typing

```
Y = [0. .48 .84 1. .91 .6 .14];
plot(Y)
```

which results in a graph on the screen:

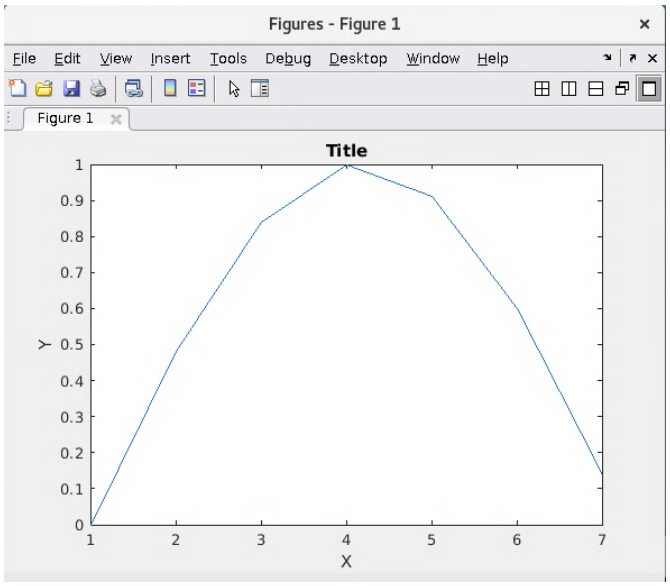


Figure 14.1.3.4.14.1.1: A Basic Plot. (CC-NC-BY-DUKE CHEM)

Notice that the data are auto-scaled and x- and y-axes are drawn. Use X Label; Y Label; and, Title from the Insert Menu to add a title and axes labels to your graph. Or, select Property Editor from the View menu. A Properties Editor box appears from which you can enter axes labels, a title and etc.

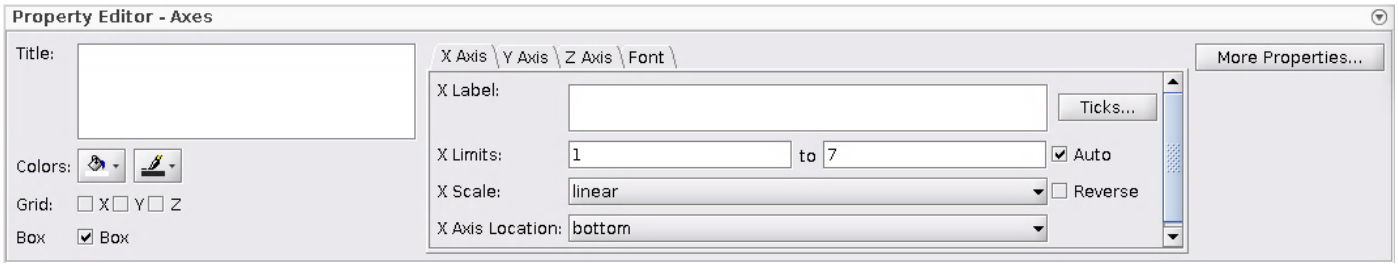


Figure 14.1.3.4.14.1.2: Property Editor. (CC-NC-BY-DUKE CHEM)

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14.1.3.4.14.2: Line Types

(b) Line types

The line types used on a graph may be controlled if the defaults are not satisfactory. Typically one does not connect data points with a line. Point plots using various symbols may be selected directly in the plot command. For example,

```
plot(X,Y,'x')
```

draws a point plot using x-mark symbols while

```
plot(X1,Y1,':',X2,Y2,'+')
```

uses a dotted line for the first curve and the plus symbol + for the second curve. Create vectors X1, Y1, X2 and Y2 and try this! Other line and point types are:

Line Type	Point Type
solid -	point .
dashed --	plus +
imag	imaginary part
dotted :	star *
dashdot -.	circle o
	x-mark x

Alternatively, the line type can be modified from within the Properties Editor window after the plot command is issued. Working with the graph above, with the Properties Editor window open, first select the arrow tool . Then click once somewhere on the actual data points. The data set will be highlighted and the Properties Editor window will change to display line properties. Under the Line menu select no line, and choose a marker from the Marker menu.

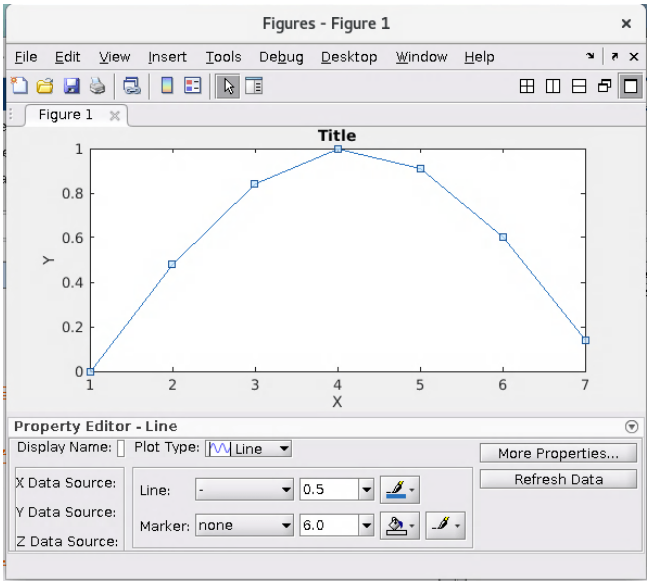


Figure 14.1.3.4.14.2.1: Line Editor.

Your graph will change accordingly. Finally, selecting More Properties from the Property Editor opens an additional options box.

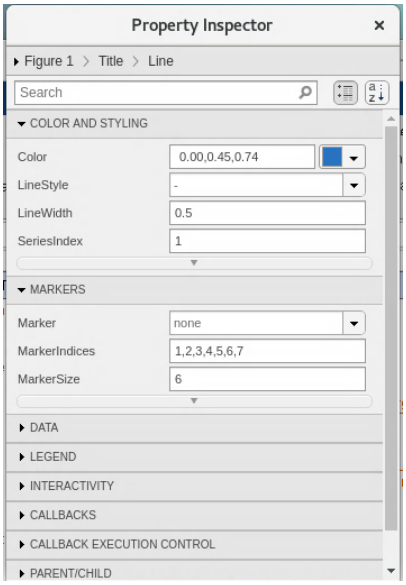


Figure 14.1.3.4.14.2.2: Property Inspector.

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14.1.3.4.14.3: Multiple Plots

The way to plot multiple lines on a single graph is to use plot with multiple arguments:

```
plot(X1,Y1,X2,Y2,...,Xn,Yn)
```

The variables X1,Y1, X2,Y2 etc. are pairs of vectors. Each x-y pair is graphed, generating multiple lines on the plot. Multiple arguments have the benefit of allowing vectors of differing lengths to be displayed on the same graph. Each pair uses a different linetype.

We can apply what we learned in the previous sections to plot simple functions. For example, to examine the behavior of the functions sin(x) and x2/100 on the interval from -15 to 15:

```
x = -15:.05:15;
y = sin(x);
z = x.^2/100;
plot(x,y,x,z)
```

which results in:

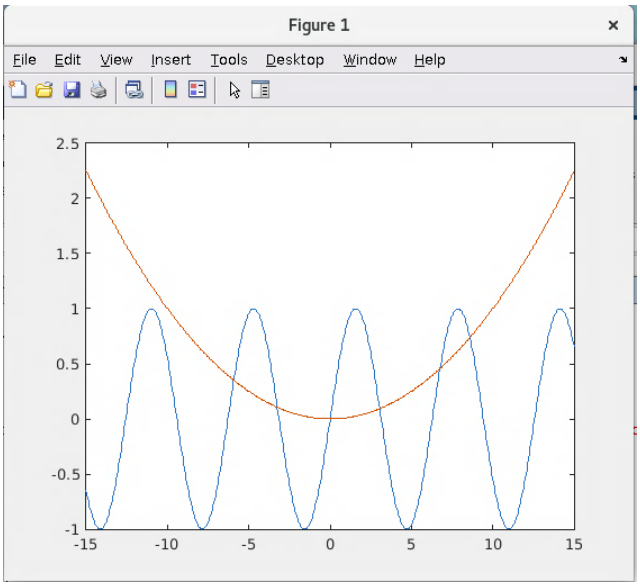


Figure 14.1.3.4.14.3.1: Multiple Plots.

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14.1.3.4.14.4: Manual Axis Scaling

In certain situations, it may be desirable to override the automatic axis scaling feature of the plot command and manually select the axis limits. Manual axis scaling is easily accomplished from the Properties Editor window mentioned above.

Alternatively, manual Axes Scaling can be accomplished from the Matlab workspace by creating a vector, V, with the following configuration

V=[X-min, X-max, Y-min, Y-max]

Working from the example graph above, let's say you wanted to scale the X axis from –5 to 5 and the Y axis from –1.5 to 1.5. Enter the following:

```
V = [-5, 5, -1.5, 1.5]
axis(V)
```

Retype the plot command plot(x,y,x,z) to observe the rescaled graph. The command **axis(V)** sets the axis scaling to the prescribed limits. If you reenter the command:

```
axis
```

autoscaling is resumed. Again, retype the command, plot(x,y,x,z), to observe the graph.

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14.1.3.4.14.5: Overlaying Plots

The command,

```
hold
```

holds the current graph on the screen. Subsequent plot commands will add to the graph, using the established axis limits and retaining the previously plotted curves. **hold** remains in effect until this command is issued again (i.e. the command **hold** can be "toggled" on and off).

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14.1.4: ESTIMATING AND REPORTING EXPERIMENTAL ERROR

Learning Objectives

After completing the readings and practice problems recommended in this module, you should be able to:

- Describe and give examples of the following types of error that effect physical measurements, and identify the types of errors that affect precision and those that affect accuracy.
  - Gross / personal error
  - Systematic error
  - Random error
  - Determinate error
  - Indeterminate error
- Describe strategies for optimizing the accuracy of physical measurements and evaluating the precision of physical measurements.
- Identify the sources of random error in a measurement.
- Propagate error using mathematics.
- Report values and their precision in the proper form (applying the rules of significant figures to correctly indicate precision).

14.1.4.1: Pre-lab Assignment

14.1.4.2: Characterizing Experimental Errors

14.1.4.3: Estimating and Reporting Error (Statistics, Propogation, and Rounding)

14.1.4.4: Least Squares Linear Regression

14.1.4.5: Rejection of Outliers (Q-test)

14.1.4.6: Guidelines for Recording and Reporting Data in your ELN

14.1.4.7: Homework Problems

14.1.4.8: References and Additional Reading

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14.1.4.1: Pre-lab Assignment

📅 **Due:** The pre-lab assignment must be completed before 1:00 PM on your scheduled lab meeting day (see syllabus schedule).

🕒 **Time:** Two to three hours in class during our first meeting. Plus, plan 4.5 hours outside of class to complete the reading and to attempt the problems in this assignment.

🎯 **Purpose**: This pre-meeting assignment is designed to help you arrive to our next meeting prepared to discuss strategies for estimating uncertainty for different types of experimental results, and for correct reporting of values and their uncertainties. Prepare to participate in the lab meeting by presenting problems on the board, answering questions from your peers, and asking your own questions.

Pre-lab assignment

In preparation for the lab meeting on Error Analysis, please do the following*:

1. **Read this entire module.**
2. **Read D.P. Shoemaker, C.W. Garland and J.W. Nibler, Experiments in Physical Chemistry, 6th Ed., McGraw Hill Co. Inc., New York, 1996, Chapter 2.**
3. **Make a sincere attempt (does not mean you must be correct) for all seven problems** in the problem set; work should be done in a way that you can track your progress and submit your work in electronic form.
4. **Submit record of your work** for all seven problems on Canvas prior to the meeting. Your pre-lab work will be graded based on work shown and evidence of sincere attempt.

Note that the textbooks referenced in this module are available in the Perkins library, and on Canvas in pdf format (or Duke students click here).
We will meet in a classroom, thus lab attire is not necessary for this session.

*For our overachievers and those who want more, recommended additional reading includes: D.A. Skoog, D.M. West, F.J. Holler and S.R. Crouch, Analytical Chemistry: An Introduction, 7th Ed., Saunders College Publishing, New York, 2000, Chapters 5-7.

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14.1.4.2: Characterizing Experimental Errors

In this course, you will need to determine the confidence in your results by doing appropriate error analysis. This section and the next are meant to review the types of experimental errors that affect accuracy and precision and to remind you of the simple methods for propagating error.

Errors That Affect Accuracy

Accuracy is how close a measure of central tendency is to its expected value, μ. We express accuracy either as an absolute error, *e*

$$e = \overline{X} - \mu \tag{14.1.4.2.1}$$

or as a percent relative error, %*e*

$$\%e = \frac{\overline{X} - \mu}{\mu} \times 100 \tag{14.1.4.2.2}$$

Although Equation 14.1.4.2.1 and Equation 14.1.4.2.2 use the mean as the measure of central tendency, we also can use the median.

> The convention for representing a statistical parameter is to use a Roman letter for a value calculated from experimental data, and a Greek letter for its corresponding expected value. For example, the experimentally determined mean is $\overline{X}$ and its underlying expected value is μ. Likewise, the experimental standard deviation is s and the underlying expected value is σ.

We identify as determinate an error that affects the accuracy of an analysis. Each source of a ***determinate error*** has a specific magnitude and sign. Some sources of determinate error are positive and others are negative, and some are larger in magnitude and others are smaller in magnitude. The cumulative effect of these determinate errors is a net positive or negative error in accuracy.

> It is possible, although unlikely, that the positive and negative determinate errors will offset each other, producing a result with no net error in accuracy.

We assign determinate errors into four categories—sampling errors, method errors, measurement errors, and personal errors—each of which we consider in this section.

Sampling Errors

A determinate sampling error occurs when our sampling strategy does not provide a us with a representative sample. For example, if we monitor the environmental quality of a lake by sampling from a single site near a point source of pollution, such as an outlet for industrial effluent, then our results will be misleading. To determine the mass of a U. S. penny, our strategy for selecting pennies must ensure that we do not include pennies from other countries.

> An awareness of potential sampling errors especially is important when we work with heterogeneous materials. Strategies for obtaining representative samples are covered in Chapter 5 of Harvey's Analytical Chemistry text on LibreTexts.

Method Errors

In any analysis the relationship between the signal, S_{total}, and the absolute amount of analyte, n_A, or the analyte's concentration, C_A, is

$$S_{total} = k_A n_A + S_{mb} \tag{14.1.4.2.3}$$

$$S_{total} = k_A C_A + S_{mb} \tag{14.1.4.2.4}$$

where k_A is the method's sensitivity for the analyte and S_{mb} is the signal from the method blank. A ***method error*** exists when our value for k_A or for S_{mb} is in error. For example, a method in which S_{total} is the mass of a precipitate assumes that k is defined by a pure precipitate of known stoichiometry. If this assumption is not true, then the resulting determination of n_A or C_A is inaccurate. We can minimize a determinate error in k_A by calibrating the method. A method error due to an interferent in the reagents is minimized by using a proper method blank.

Measurement Errors

The manufacturers of analytical instruments and equipment, such as glassware and balances, usually provide a statement of the item's maximum ***measurement error***, or ***tolerance***. For example, a 10-mL volumetric pipet (Figure 3.2.1) has a tolerance of ±0.02 mL, which means the pipet delivers an actual volume within the range 9.98–10.02 mL at a temperature of 20 °C. Although we express this tolerance as a range, the error is determinate; that is, the pipet's expected volume, μ, is a fixed value within this stated range.

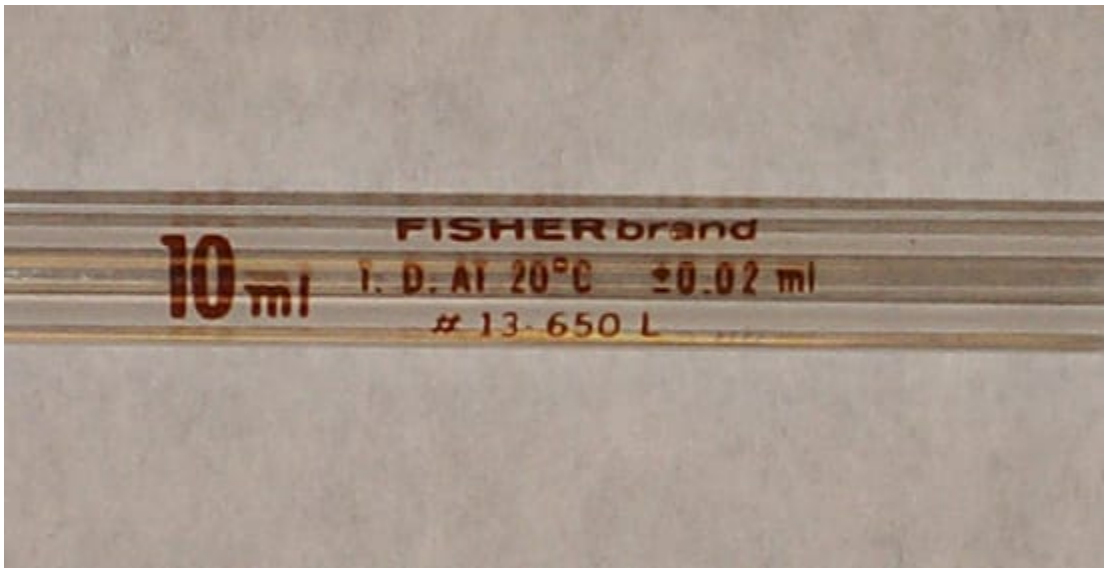


Figure 3.2.1 : Close-up of a 10-mL volumetric pipet showing that it has a tolerance of ±0.02 mL at 20 °C.

Volumetric glassware is categorized into classes based on its relative accuracy. **Class A glassware** is manufactured to comply with tolerances specified by an agency, such as the National Institute of Standards and Technology or the American Society for Testing and Materials. The tolerance level for Class A glassware is small enough that normally we can use it without calibration. The tolerance levels for **Class B glassware** usually are twice that for Class A glassware. In other words, Class B is less accurate. Other types of volumetric glassware, such as beakers and graduated cylinders, are not used to measure volume accurately. Table 3.2.1 provides a summary of typical measurement errors for Class A volumetric glassware. Tolerances for digital pipets and for balances are provided in Table 3.2.2 and Table 3.2.3 .

Tolerance Limits for Class A Volumetric Glassware

*Table 3.2.1 : Measurement Errors for **Class A Volumetric Glassware***

Volumetric Pipets		Volumetric Flasks		Burets	
Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)
1	± 0.006	5	± 0.02	10	± 0.02
2	± 0.006	10	± 0.02	25	± 0.03
5	± 0.01	25	± 0.03	50	± 0.05
10	± 0.02	50	± 0.05		
20	± 0.03	100	± 0.08		
25	± 0.03	250	± 0.12		
50	± 0.05	500	± 0.20		
100	± 0.08	1000	± 0.30		
		2000	± 0.50		

Tolerance limits for Digital Pipettes

Table 3.2.2 : Measurement Errors for Digital Pipets

Pipet Range	Volume (mL or μL)	Percent Measurement Error
10–100 μL	10	$\pm 3.0\%$
	50	$\pm 1.0\%$
	100	$\pm 0.8\%$
100–1000 μL	100	$\pm 3.0\%$
	500	$\pm 1.0\%$
	1000	$\pm 0.6\%$
1–10 mL	1	$\pm 3.0\%$
	5	$\pm 0.8\%$
	10	$\pm 0.6\%$

The tolerance values for the volumetric glassware in Table 3.2.1 are from the ASTM E288, E542, and E694 standards. The measurement errors for the digital pipets in Table 3.2.2 are from www.eppendorf.com.

Tolerance Limits for Some Common Balances

Table 3.2.3 : Measurement Errors for Selected Balances

Balance	Capacity (g)	Measurement Error
Precisa 160M	160	± 1 mg
A & D ER 120M	120	± 0.1 mg
Metler H54	160	± 0.01 mg

We can minimize a determinate measurement error by calibrating our equipment. Balances are calibrated using a reference

weight whose mass we can trace back to the SI standard kilogram. Volumetric glassware and digital pipets are calibrated by determining the mass of water delivered or contained and using the density of water to calculate the actual volume. It is never safe to assume that a calibration does not change during an analysis or over time. One study, for example, found that repeatedly exposing volumetric glassware to higher temperatures during machine washing and oven drying, led to small, but significant changes in the glassware's calibration [Castanheira, I.; Batista, E.; Valente, A.; Dias, G.; Mora, M.; Pinto, L.; Costa, H. S. *Food Control* **2006**, *17*, 719–726]. Many instruments drift out of calibration over time and may require frequent recalibration during an analysis.

Personal Errors

Finally, analytical work is always subject to ***personal error***, examples of which include the ability to see a change in the color of an indicator that signals the endpoint of a titration, biases, such as consistently overestimating or underestimating the value on an instrument's readout scale, failing to calibrate instrumentation, and misinterpreting procedural directions. You can minimize personal errors by taking proper care.

Identifying Determinate Errors

Determinate errors often are difficult to detect. Without knowing the expected value for an analysis, the usual situation in any analysis that matters, we often have nothing to which we can compare our experimental result. Nevertheless, there are strategies we can use to detect determinate errors.

The magnitude of a constant ***determinate error*** is the same for all samples and is more significant when we analyze smaller samples. Analyzing samples of different sizes, therefore, allows us to detect a constant determinate error. For example, consider a quantitative analysis in which we separate the analyte from its matrix and determine its mass. Let's assume the sample is 50.0% w/w analyte. As we see in Table 3.2.4 , the expected amount of analyte in a 0.100 g sample is 0.050 g. If the analysis has a positive constant determinate error of 0.010 g, then analyzing the sample gives 0.060 g of analyte, or an apparent concentration of 60.0% w/w. As we increase the size of the sample the experimental results become closer to the expected result. An upward or downward trend in a graph of the analyte's experimental concentration versus the sample's mass (Figure 3.2.2) is evidence of a constant determinate error.

Table 3.2.4 : Effect of a Constant Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Constant Error (g)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	0.010	0.060	60.0
0.200	0.100	0.010	0.110	55.0
0.400	0.200	0.010	0.210	52.5
0.800	0.400	0.010	0.410	51.2
1.600	0.800	0.010	0.810	50.6

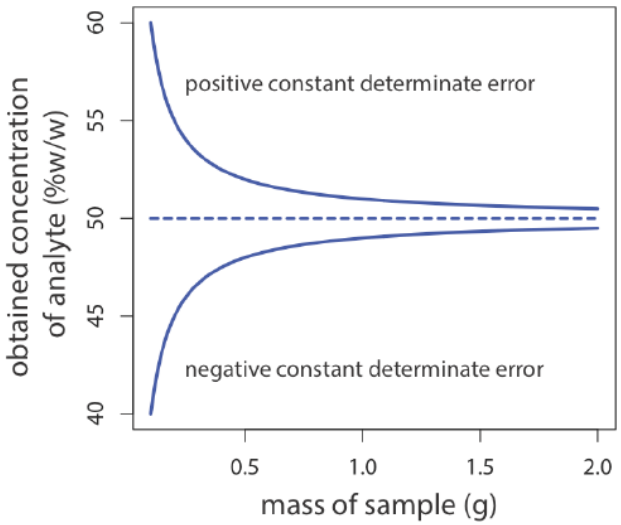


Figure 3.2.2 : Effect of a constant positive determinate error of +0.01 g and a constant negative determinate error of –0.01 g on the determination of an analyte in samples of varying size. The analyte's expected concentration of 50% w/w is shown by the dashed line.

A ***proportional determinate error***, in which the error's magnitude depends on the amount of sample, is more difficult to detect because the result of the analysis is independent of the amount of sample. Table 3.2.5 outlines an example that shows the effect of a positive proportional error of 1.0% on the analysis of a sample that is 50.0% w/w in analyte. Regardless of the sample's size, each analysis gives the same result of 50.5% w/w analyte.

Table 3.2.5 : Effect of a Proportional Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Proportional Error (%)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	1.00	0.0505	50.5
0.200	0.100	1.00	0.101	50.5
0.400	0.200	1.00	0.202	50.5
0.800	0.400	1.00	0.404	50.5
1.600	0.800	1.00	0.808	50.5

One approach for detecting a proportional determinate error is to analyze a standard that contains a known amount of analyte in a matrix similar to our samples. Standards are available from a variety of sources, such as the National Institute of Standards and Technology (where they are called Standard Reference Materials) or the American Society for Testing and Materials. Table 3.2.6 , for example, lists certified values for several analytes in a standard sample of *Gingko biloba* leaves. Another approach is to compare our analysis to an analysis carried out using an independent analytical method that is known to give accurate results. If the two methods give significantly different results, then a determinate error is the likely cause.

Table 3.2.6 : Certified Concentrations for SRM 3246: Gingko bilbo (Leaves)

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
Flavonoids/Ginkgolide B (mass fraction in mg/g)	Qurecetin	2.69 ± 0.31
	Kaempferol	3.02 ± 0.41
	Isorhamnetin	$0.517 \pm 0.0.99$
	Total Aglycones	6.22 ± 0.77
Selected Terpenes (mass fraction in mg/g)	Ginkgolide A	0.57 ± 0.28
	Ginkgolide B	0.470 ± 0.090

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
	Ginkgolide C	0.59 ± 0.22
	Ginkgolide J	0.18 ± 0.10
	Bilobalide	1.52 ± 0.40
	Total Terpene Lactones	3.3 ± 1.1
Selected Toxic Elements (mass fraction in ng/g)	Cadmium	20.8 ± 1.0
	Lead	995 ± 30
	Mercury	23.08 ± 0.17

The primary purpose of this Standard Reference Material is to validate analytical methods for determining flavonoids, terpene lactones, and toxic elements in *Ginkgo biloba* or other materials with a similar matrix. Values are from the official Certificate of Analysis available at www.nist.gov.

Constant and proportional determinate errors have distinctly different sources, which we can define in terms of the relationship between the signal and the moles or concentration of analyte (Equation 14.1.4.2.3 and Equation 14.1.4.2.4). An invalid method blank, S_{mb}, is a constant determinate error as it adds or subtracts the same value to the signal. A poorly calibrated method, which yields an invalid sensitivity for the analyte, k_A, results in a proportional determinate error.

Errors that Affect Precision

Precision is a measure of the spread of individual measurements or results about a central value, which we express as a range, a standard deviation, or a variance. Here we draw a distinction between two types of precision: repeatability and reproducibility. ***Repeatability*** is the precision when a single analyst completes an analysis in a single session using the same solutions, equipment, and instrumentation. ***Reproducibility***, on the other hand, is the precision under any other set of conditions, including between analysts or between laboratory sessions for a single analyst. Since reproducibility includes additional sources of variability, the reproducibility of an analysis cannot be better than its repeatability.

The ratio of the standard deviation associated with reproducibility to the standard deviation associated with repeatability is called the Horowitz ratio. For a wide variety of analytes in foods, for example, the median Horowtiz ratio is 2.0 with larger values for fatty acids and for trace elements; see Thompson, M.; Wood, R. "The 'Horowitz Ratio'–A Study of the Ratio Between Reproducibility and Repeatability in the Analysis of Foodstuffs," *Anal. Methods*, **2015**, *7*, 375–379.

Errors that affect precision are indeterminate and are characterized by random variations in their magnitude and their direction. Because they are random, positive and negative ***indeterminate errors*** tend to cancel, provided that we make a sufficient number of measurements. In such situations the mean and the median largely are unaffected by the precision of the analysis.

Sources of Indeterminate Error

We can assign indeterminate errors to several sources, including collecting samples, manipulating samples during the analysis, and making measurements. When we collect a sample, for instance, only a small portion of the available material is taken, which increases the chance that small-scale inhomogeneities in the sample will affect repeatability. Individual pennies, for example, may show variations in mass from several sources, including the manufacturing process and the loss of small amounts of metal or the addition of dirt during circulation. These variations are sources of indeterminate sampling errors.

During an analysis there are many opportunities to introduce indeterminate method errors. If our method for determining the mass of a penny includes directions for cleaning them of dirt, then we must be careful to treat each penny in the same way. Cleaning some pennies more vigorously than others might introduce an indeterminate method error.

Finally, all measuring devices are subject to indeterminate measurement errors due to limitations in our ability to read its scale. For example, a buret with scale divisions every 0.1 mL has an inherent indeterminate error of ±0.01–0.03 mL when we estimate the volume to the hundredth of a milliliter (Figure 3.2.3).

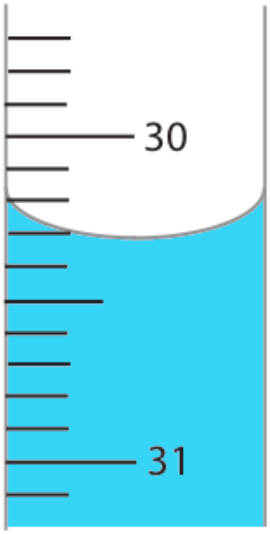


Figure 3.2.3 : Close-up of a buret showing the difficulty in estimating volume. With scale divisions every 0.1 mL it is difficult to read the actual volume to better than ±0.01–0.03 mL.

Evaluating Indeterminate Error

Indeterminate errors associated with our analytical equipment or instrumentation generally are easy to estimate if we measure the standard deviation for several replicate measurements, or if we monitor the signal's fluctuations over time in the absence of analyte (Figure 3.2.4) and calculate the standard deviation. Other sources of indeterminate error, such as treating samples inconsistently, are more difficult to estimate.

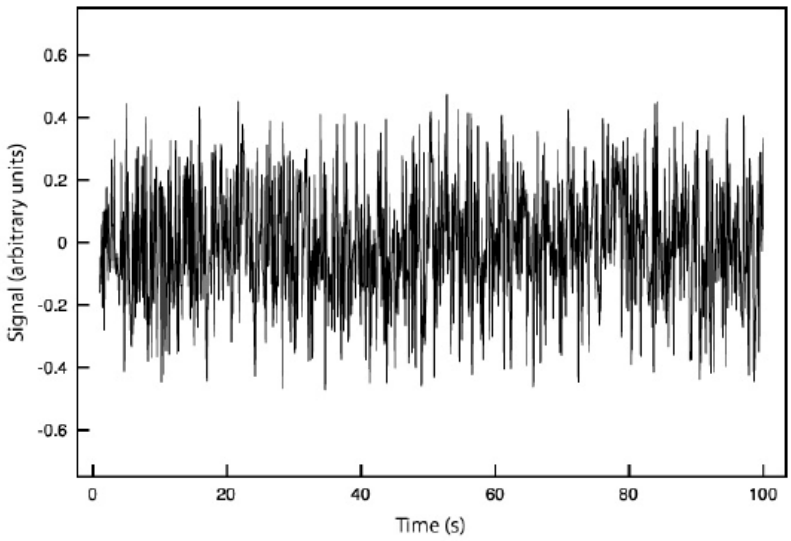


Figure 3.2.4 : Background noise in an instrument showing the random fluctuations in the signal.

Error and Uncertainty

Analytical chemists make a distinction between error and uncertainty [Ellison, S.; Wegscheider, W.; Williams, A. *Anal. Chem.* **1997**,

69, 607A–613A]. ***Error*** is the difference between a single measurement or result and its expected value. In other words, error is a measure of ***bias***. As discussed earlier, we divide errors into determinate and indeterminate sources. Although we can find and correct a source of determinate error, the indeterminate portion of the error remains.

Uncertainty expresses the range of possible values for a measurement or result. Note that this definition of uncertainty is not the same as our definition of precision. We calculate precision from our experimental data and use it to estimate the magnitude of indeterminate errors. Uncertainty accounts for all errors—both determinate and indeterminate—that reasonably might affect a measurement or a result. Although we always try to correct determinate errors before we begin an analysis, the correction itself is subject to uncertainty.

Here is an example to help illustrate the difference between precision and uncertainty. Suppose you purchase a 10-mL Class A pipet from a laboratory supply company and use it without any additional calibration. The pipet's tolerance of ±0.02 mL is its uncertainty because your best estimate of its expected volume is 10.00 mL ± 0.02 mL. This uncertainty primarily is determinate. If you use the pipet to dispense several replicate samples of a solution and determine the volume of each sample, the resulting standard deviation is the pipet's precision. Table 3.2.8 shows results for ten such trials, with a mean of 9.992 mL and a standard deviation of ±0.006 mL. This standard deviation is the precision with which we expect to deliver a solution using a Class A 10-mL pipet. In this case the pipet's published uncertainty of ±0.02 mL is worse than its experimentally determined precision of ±0.006 ml. Interestingly, the data in Table 3.2.8 allows us to calibrate this specific pipet's delivery volume as 9.992 mL. If we use this volume as a better estimate of the pipet's expected volume, then its uncertainty is ±0.006 mL. As expected, calibrating the pipet allows us to decrease its uncertainty [Kadis, R. *Talanta* **2004**, *64*, 167–173].

Table 3.2.8 : Experimental Results for Volume Dispensed by a 10–mL Class A Transfer Pipet

Replicate	Volume (ml)	Replicate	Volume (mL)
1	10.002	6	9.983
2	9.993	7	9.991
3	9.984	8	9.990
4	9.996	9	9.988
5	9.989	10	9.999

Adapted from 4.2: Characterizing Experimental Errors by David Harvey.

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14.1.4.3: Estimating and Reporting Error (Statistics, Propogation, and Rounding)

In many physical chemistry experiments, the goal is to obtain numerical results by taking measurements and calculating averages or applying theoretical formulas. However, simply producing a number isn't enough – it's essential to evaluate its quality. How accurate is the result? Accuracy indicates the level of uncertainty associated with the measurement. Overstating accuracy without proper justification can be misleading, while understating it can undervalue the result and lead to wasted effort and resources.

This page summarizes two main ways to approach the estimation of uncertainty. You will practice when and how to use each strategy by completing the problem set at the end of this module.

1. **Strategy 1: Statistical Analyses** can be used to estimate uncertainty when there are multiple replicates of the same measurement(s).
2. **Strategy 2: Propagation of Uncertainties** can be used to estimate uncertainty when using measured values in a function to calculate another numerical value (the vlaue of the function).

A major goal of this module is for you to learn when and how to apply these equations to perform statistical analysis or propagate uncertainties through a function. This skill will be required in nearly every future module in this course.

A summary of useful information and equations is below.

1. Statistical Analyses (on replicate measurements):

Average or mean: The average (or mean) of N measurements on the variable x is:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{14.1.4.3.1}$$

Standard deviation (S) is the spread around the mean of several replicate measurements. It has the same units as the measurement and is commonly used to report uncertainty (see Skoog Ch. 6 p 126)

$$S = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}} \tag{14.1.4.3.2}$$

Variance (S^2) is the dispersion between data points. The units are the square of the measured units.

The **Confidence Limits (CL)** are the values that define the confidence interval (which is the bounds about which an experimental value should be located with a given probability). The confidence limit is useful for small sample sizes. A common confidence limit is the 95% confidence limit, and its value is given by the following (see Skoog Ch7 pg 150 and Shoemaker Ch 2 eq 34).

$$CL_{0.95} = t_{0.95}S_m = t_{0.95}\frac{S}{\sqrt{N}} \tag{14.1.4.3.3}$$

or more generally

$$CL = \bar{x} \pm \frac{tS}{\sqrt{N}} \tag{14.1.4.3.4}$$

where t is the critical t value (from Student's t test) that depends on the degrees of freedom and the given probability. A table of critical t values can be found online. (See also Shoemaker Ch 2, Table 3)

2. Propagation of uncertainties (for values determined from a function):

Note on symbolism

I have chosen to use symbolism that is partly, but not completely, consistent with Shoemaker text. The following symbols are used on this page:

- **Values** are symbolized as x , y, z (these are values that have some uncertainty associated with them).
- The value of a **Function** is symbolized as F.
- **Uncertainty** in the values x, y, z, F are symbolized as u_x, u_y, u_z, u_F, respectively.*
- Coefficients or absolute constants are symbolized by a, b, c.

*u_x is used here to indicate the uncertainty in value x. Shoemaker uses $\Delta(x)$, which is a bit confusing, since it looks a lot like Δx which means "change in x" in many science fields. Ugh... u_x feels better to me, so I use it here.

Using partial derivatives

When using values (x , y, z) to calcuate the value of a function (F), we must propagate uncertainties of each operand (u_x, u_y, u_z,) to determine the uncertainty in the function's value u_F. This is accomplished by taking the square root of the sum of the squares of the partial derivative of the function with respect to each variable (eg partial derivative with respect to x is $\frac{\partial F}{\partial x}$), multiplied by the uncertainty in that variable (eg uncertainty in x is u_x, and the square of the uncertainty is u_x^2. In mathematical form, this is given below (from Shoemaker Ch 2 p 56, eq 54).

$$u_F^2 = \left(\frac{\partial F}{\partial x}\right)^2 u_x^2 + \left(\frac{\partial F}{\partial y}\right)^2 u_y^2 + \left(\frac{\partial F}{\partial z}\right)^2 u_z^2 + \ldots \tag{14.1.4.3.5}$$

It is convenient to rearrange this equation as follows to give the uncertainty in the value derived from the function:

$$u_F = \sqrt{\left(\frac{\partial F}{\partial x}\right)^2 u_x^2 + \left(\frac{\partial F}{\partial y}\right)^2 u_y^2 + \left(\frac{\partial F}{\partial z}\right)^2 u_z^2 + \ldots} \tag{14.1.4.3.6}$$

Simpler shortcuts:

In some cases, there are shortcuts that allow you to approximate uncertainties without taking the partial derivatives. In the examples below, assume that a, b, c are constants and x , y, z are variables with associated uncertaintyu_x, u_y, u_z:

For functions with only addition and subtraction of values with associated uncertainty (eg $F = ax \pm by \pm cz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 55)

$$u_F = \sqrt{a^2u_x^2 + b^2u_y^2 + c^2u_z^2} \tag{14.1.4.3.7}$$

For functions that involve only multiplication and division (eg $F = axyz$ **or** $F = axy/z$ **or** $F = a/xyz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 56)

$$u_F = F\sqrt{\frac{u_x^2}{x^2} + \frac{u_y^2}{y^2} + \frac{u_z^2}{z^2}} \tag{14.1.4.3.8}$$

For functions that involve taking a variable to the power of a constant (eg $F = ax^n$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 57)

$$u_F = F\sqrt{n^2\frac{u_x^2}{x^2}} \rightarrow u_F = Fn\frac{u_x}{x} \tag{14.1.4.3.9}$$

For functions where a variable is an exponent (eg $F = ae^x$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 58)

$$u_F = \sqrt{a^2e^{2x}u_x^2} \rightarrow u_F = Fu_x \tag{14.1.4.3.10}$$

For functions taking the logarithm of a variable (eg $F = a\ln(x)$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 59)

$$u_F = \sqrt{\frac{a^2}{x^2}u_x^2} \rightarrow u_F = a\frac{u_x}{x} \tag{14.1.4.3.11}$$

3. Reporting Numeric Results

All numeric results in this course should be reported with explicit statement of uncertainty. The following format is expected:

$$\text{Numeric Value } \pm \text{Uncertainty} \tag{14.1.4.3.12}$$

In your written assignments for this course use the following guidelines when reporting a "final" numeric value. You will be required to use your *best judgement* and to provide a *written justification* of your logic for reporting all final values. More detailed information is found below the guidelines and also in the Shoemaker text.

Guidelines for reporting final numerical values:

- Rules for reporting significant figures should be followed.
- The number of useful decimal places in the uncertainty should match the number of decimal places reported in the value.
- The certainty of a numeric value determined from a function cannot be be more than the certainty of its operands.

A summary of rules for reporting significant Figures (from Shoemaker Ch 2)

The following rules apply only for reporting the *final* value, not for intermediate rounding steps during calculation. In general, do not round values during the calculation process if it can be avoided. However, if you must round prior to completing a calculation, then retain *at least one digit more than would be considered "significant"*, and the more the better.

Rules for Rounding Final Values:

Follow the following rules depending on the digit immediately to the right of the place you are rounding. The examples below are rounding to the place underlined, and **the digit immediately to the right is bolded**.

a. Increase the last retained digit by 1 if the nearest dropped digit is more than 5, or if it is 5 followed by any non-zero digits:
   - Examples:
     6.78**9** rounds to 6.79
     54.91**2**3 rounds to 54.9
b. Leave the last retained digit unchanged if the nearest dropped digit is less than 5:
   - Examples:
     2.34**6** rounds to 2.35
     0.212**3** rounds to 0.21
c. If the leftmost digit to be dropped is 5 followed by no digits except zero, then increase the last retained digit by 1 if it is odd, and leave it unchanged if it is even:
   - Examples:
     15.32**5** rounds to 15.32
     15.33**5** rounds to 15.34
d. There are times when you should retain an extra digit so that your reported uncertainty is reasonable.

Rules for tracking significant figures for calculated values

Addition: When adding numeric values, the result's precision is limited by the least precise value involved. The number of decimal places in the result should match the fewest decimal places in any component. For example:

$$\begin{aligned} &15.4 \\ +&2.87 \\ +&7.621 \\ =&25.916 \rightarrow 25.9 \end{aligned} \tag{14.1.4.3.13}$$

Subtraction: When subtracting, the result's precision is limited by the least precise value involved, and the precision of the result will always be less than that of the operands. For example:

$$\begin{aligned} &289.461 \\ -&288.58 \\ &0.881 \rightarrow 0.88 \end{aligned} \tag{14.1.4.3.14}$$

Let's do an analysis to illustrate what this means. In the example above, let's assume an uncertainty of ± 3 in the rightmost digit of each number. Based on this assumption, the least precise operand has uncertainty of ~ 0.01%, while the final reported value has an uncertainty of 3.4%!

When multiplying and dividing: In multiplication and division, the precision of the result is limited by the least precise number involved. The number of significant figures in the result should align with the component having the fewest. ***Note that relative precision isn't solely dependent on the number of significant figures;*** for instance, 99 with two significant figures is approximately as precise as 101 with three. When unsure, do an analysis of the relative uncertainty, and if the uncertinties are approximately equal, use the larger number of significant figures.

Conventions for Reporting and Interpreting Reported Values

1. Numerical values are typically considered uncertain in the last digit by ±3 or more, with perhaps slight uncertainty in the next-to-last digit by up to ±2.
2. If the last digit to be retained is a one or two, an additional digit is retained so that precision is not inappropriately reported due to rounding.

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14.1.4.4: Least Squares Linear Regression

Your experimental data will usually be examined in graphic form, which can be more instructive than tabulated data. In any graphic presentation, be sure to plot your independent variable on the abscissa (x-axis) and the dependent variable on the ordinate (y-axis).

If the data are presented in graphic form, the usual procedure is to fit the best curve through the experimental points. As Brownlee[3] puts it,

> "When an investigator observes simultaneously two variables, x and y, usually with good reason he plots the observations on a graph. If there is any sign of an association, he is usually seized with the impulse to fit a line, usually a straight line or, rather infrequently, a parabola or cubic."

When we are "seized with the impulse" to fit a straight line curve the process of curve fitting is called linear regression. We assume that the deviations of the dependent variable y are distributed normally (that is, a Gaussian distribution). This assumption is not required for the determination of the least squares parameters, but it is necessary for construction of confidence intervals or for tests of hypotheses about the parameters. The parameters obtained by least squares under these conditions are unbiased and provide the best estimates of the curve fitting parameters.

Most of the experimental data that you will encounter this semester will have a simple functional form, or can be manipulated in such a way as to assume a simple form. We shall assume here that our data follows a linear relationship. For example, consider a gas that is thought to follow the equation of state

$$\begin{gathered} \mathrm{Z} \equiv \frac{\mathrm{PV}}{\mathrm{nRT}} = \mathrm{B}_0 + \mathrm{B}_1\mathrm{P} \\ \mathrm{y} = \mathrm{a} + \mathrm{bx} \end{gathered} \tag{14.1.4.4.1}$$

Measurements of Z, called the compressibility factor, are made at each of a series of pressures in an effort to determine B_0 andB_0. The least squares approach can be used to determine the slope (b, orB_1) and y-intercept (a, or B_0) which define the best straight line that can be drawn through the data. In simple linear regression analysis, it is assumed that all the error in the measurement lies in the dependent variable (y). This is equivalent to assuming that the precision of the determination of the independent variable (x) is considerable higher than that of y. The measured value of some quantity (y_i) will differ from the value predicted by a linear equation ($y = a + bx$) by an amount r_i called the residual.

$$r_i = y_i - a - bx \tag{14.1.4.4.2}$$

The least squares approach identifies the best straight line as the one for which R, the sum of the squares of the residuals, has the smallest value:

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} (y_i - a - bx_i)^2 \tag{14.1.4.4.3}$$

The arrows in Figure 4 represent the residuals, and all of them are equally weighted.

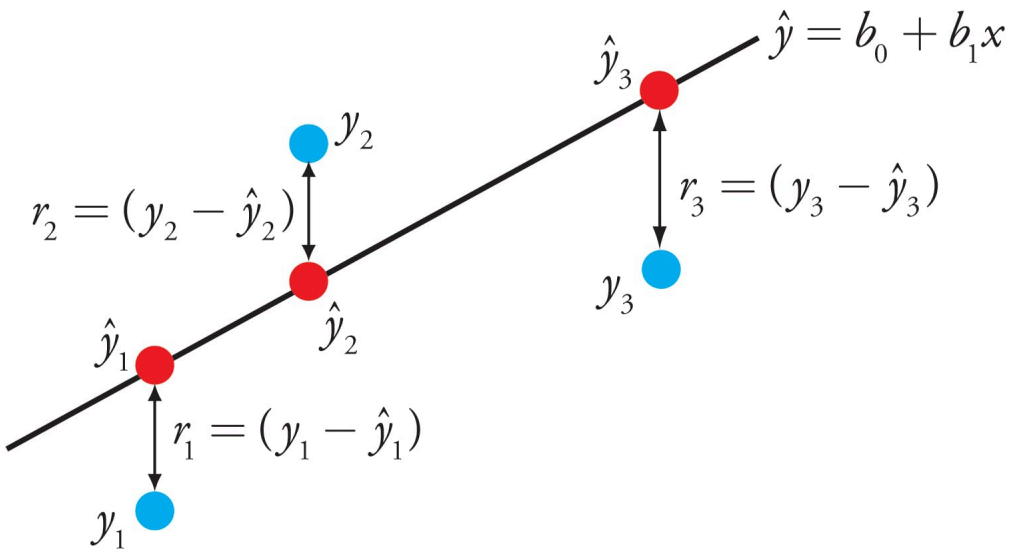


Figure 14.1.4.4.1: Least Squares Linear Regression: *Illustration showing the evaluation of a linear regression in which we assume that all uncertainty is the result of indeterminate errors affecting y. The points in blue, y_i, are the original data and the points in red, $\hat{y}_i$, are the predicted values from the regression equation, $\hat{y} = b_0 + b_1 x$. The smaller the total residual error, the better the fit of the straight-line to the data* (source)

We want to minimize the sum of the squares of the residuals. That is, we want to make *least* the sum of *squares* of residuals, and, thus, the name of the procedure. Since this is a minimization problem, we require that R be as small as possible with respect to a and b by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial a}\right)_b = -2\sum(y_i - a - bx_i) = 0 \tag{14.1.4.4.4}$$
$$\left(\frac{\partial R}{\partial b}\right)_a = -2\sum((y_i - a - bx_i)(x_i)) = 0$$

Solving equations 14.1.4.4.4 simultaneously, we obtain

$$a = \frac{(\sum x_i^2)(\sum y_i) - (\sum x_i)(\sum x_i y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{14.1.4.4.5}$$

$$b = \frac{N(\sum x_i y_i) - (\sum x_i)(\sum y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{14.1.4.4.6}$$

While we ultimately want to fit the data to $y_i = a + bx_i$ for a series i of N points, the theoretical development is much easier if we use $y_i = c + b(x_i - \overline{x})$ where obviously a and c are related by $a = c - b\overline{x}$, and where $\overline{x}$ is simply the mean of the x data, $n\overline{x} = \sum_{i=1}^{N} x_i$. This designation of variables is better because "it turns out" that in this approach the parameters b and c are independent, their variances are independent, and the formulas to transform to the parameters a and b are simple. Again, we want to minimize the sum of the squares of the residuals $r_i = y_i - c - b(x_i - \overline{x})$, R.

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} [y_i - (c + b(x_i - \overline{x}))]^2 \tag{14.1.4.4.7}$$

Now we require that R be as small as possible with respect to b and c by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial c}\right)_b = -2\sum (y_i - c - b(x_i - \overline{x})) = 0 \tag{14.1.4.4.8}$$
$$\left(\frac{\partial R}{\partial b}\right)_c = -2\sum ((y_i - c - b(x_i - \overline{x}))(x_i - \overline{x})) = 0$$

These two equations are readily rewritten as

$$\begin{aligned} \sum y_i &= \sum c + \sum b\left(x_i - \overline{x}\right) \\ \sum y_i\left(x_i - \overline{x}\right) &= \sum c\left(x_i - \overline{x}\right) + \sum b\left(x_i - \overline{x}\right)^2 \end{aligned} \tag{14.1.4.4.9}$$

which, since $\sum\left(x_i - \overline{x}\right) = 0$, simplify to

$$\begin{aligned} c &= \frac{\sum y_i}{N} = -\overline{y} \\ b &= \frac{\sum y_i\left(x_i - \overline{x}\right)}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{14.1.4.4.10}$$

The knowledge of c and b then allows us to determine the parameter, a, $a = c - b\overline{x} = \overline{y} - b\overline{x}$, a particularly simple relation.

The variance and standard deviation of N data points was introduced previously. The appropriate treatment of the parameters c and b in the least squares procedure results in

$$\begin{aligned} V[c] &= \frac{s^2}{N} \\ V[b] &= \frac{s^2}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{14.1.4.4.11}$$

where

$$s^2 = \frac{1}{N-2}\sum\left(y_i - c - b\left(x_i - \overline{x}\right)\right)^2 = \frac{1}{N-2}\sum\left(y_i - a - bx_i\right)^2 = \frac{R_{min}}{N-2} \tag{14.1.4.4.12}$$

Because c and b are independent quantities, it can be shown that

$$\begin{aligned} V[a] &= V[c] + \overline{x}^2 V[b] \\ &= \frac{s^2}{N} + \overline{x}^2\frac{s^2}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{14.1.4.4.13}$$

The standard deviations of a and b, σ_a and σ_b, are then obtained by taking the square roots of V[a] and V[b].

Another statistic that is sometimes used is the *correlation coefficient,* r. It is given by the expression

$$r = \frac{N\sum x_i y_i - \sum x_i \sum y_i}{\sqrt{\left(N\sum x_i^2 - \left(\sum x_i\right)^2\right)\left(N\sum y_i^2 - \left(\sum y_i\right)^2\right)}} \tag{14.1.4.4.14}$$

When the absolute value of r is close to unity the correlation between the y and x data is good, when it is close to zero the correlation is poor. Because the correlation coefficient is sometimes hard to interpret, it is usually better to work with the standard deviations of the regression parameters, σ_a and σ_b.

Linear regression is a powerful tool that takes the guesswork out of obtaining best fit information. However, like all mathematical tools, it must be used with caution. While the standard deviations and the correlation coefficient give indications of the goodness of the fit, there is no substitute for graphing the data and looking at the result. Since the errors are assumed to be random, the y_i values should be scattered about the best fit straight line in a random fashion. The residuals should likewise be either positive or negative (and sum to zero) without any pattern. If the data show a pattern of curvature, it is possible that the results do not conform to the linear model proposed. A linear regression is *not* valid in this case. You should also be alert to the effects of systematic errors, which may change the slope or the intercept without affecting the linearity of the data.

Linear regression of the type discussed above relies on a number of critical assumptions. Among the most important is that all the uncertainty in each of the y values is the same. If the form of the equation required to provide a linear relationship produces an independent variable that contains a significant uncertainty, the set of conditions that produced the minimum in the residuals of the line may not be the set that actually minimizes the uncertainty in the data. In this case, a "non-linear" least squared technique such as simplex is recommended.

Note

In this course, you can use the MatLab lsq.m script to perform least squares analysis. The equations given above are included in the lsq script.

Weighted Least Squares Analysis

When measurements of the dependent variable incur different uncertainties, a ***weighted*** least squares technique should be used. In this approach, each residual ri is divided by a factor proportional to its uncertainty ε_{y_i}. Then R, the sum of the squares of the residuals, becomes

$$R = \sum_{i=1}^{N} \frac{r_i^2}{\varepsilon_{y_i^2}} = \sum_{i=1}^{N} \frac{1}{\varepsilon_{y_i^2}} (y_i - a - bx_i)^2 \tag{14.1.4.4.15}$$

Using the same minimization techniques described above, the slope and intercept for weighted least squares become

$$a = \frac{\sum \frac{x_i^2}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2} \right)^2} \tag{14.1.4.4.16}$$

$$b = \frac{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2} \right)^2} \tag{14.1.4.4.17}$$

Weighted least squares has utility in a number of applications in the physical chemistry laboratory. One common situation arises when a linear equation requires the log of a measured quantity to be the dependent variable. Consider for example, the measurement of vapor pressure. Most pressure sensing devices will provide a constant error in the measurement of P. If the dependent variable to be plotted is lnP, however, its uncertainty is not constant but decreases as P increases. Thus,

$$\varepsilon_{lnP} = \frac{\partial lnP}{\partial P} \varepsilon_P = \frac{\varepsilon_P}{P} \tag{14.1.4.4.18}$$

An appropriate weighting factor in this case would be $\varepsilon_{y_i} = \frac{1}{P}$.

When you use Matlab for data analysis this semester, the command **lsq(x,y)** will be used for least squares analysis of x, y data, and the command **wtlsq(x,y)** will be used for weighted least squares analysis. In the latter case, you will be asked for a weighting factor, e. In either case, the program will output the least squares slope, y-intercept, correlation coefficient, standard deviation of the slope, and standard deviation of the intercept.

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14.1.4.5: Rejection of Outliers (Q-test)

In a set of collected data, there may be one or more values that deviate markedly from the trend of the others; in other words, there may be one or more data points that seem suspicious. If a measurement appears suspicious, we need evidence before deciding that it is statistically discordant with the rest of the data. One tool for doing this is the **Q-test**.

> **You should not reject a piece of data that seems suspect until you perform a Q-test**.

In a set of data of three to ten measurements, the Q-test can be performed on a single suspicious data point as follows:

$$Q_{exp} \equiv \frac{|\text{ (suspected outlier's value) } - \text{ (value closest to it) }|}{\text{(highest value) } - \text{ (lowest value)}} \tag{14.1.4.5.1}$$

The following table provides critical values for $Q_{critical}(\alpha, n)$, where:

- α is the probability of incorrectly rejecting the suspected outlier,
- n is the number of samples in the data set.

Table 14.1.4.5.1*: Critical Values for Dixon's Q-Test*

$\frac{\alpha \longrightarrow}{\text{no. of samples}\downarrow}$	$Q_{critical}$ $\alpha = 0.1$ **(90% confidence limit)**	$Q_{critical}$ $\alpha = 0.05$ **(95% confidence limit)**	$Q_{critical}$ $\alpha = 0.04$ **(96% confidence limit)**	$Q_{critical}$ $\alpha = 0.02$ **(98% confidence limit)**	$Q_{critical}$ $\alpha = 0.01$ **(99% confidence limit)**
n = 3	0.941	0.970	0.976	0.988	0.994
n = 4	0.765	0.829	0.846	0.889	0.926
n = 5	0.642	0.710	0.729	0.780	0.821
n = 6	0.560	0.625	0.644	0.698	0.740
n = 7	0.507	0.568	0.586	0.637	0.680
n = 8	0.468	0.526	0.543	0.590	0.634
n = 9	0.437	0.493	0.510	0.555	0.598
n = 10	0.412	0.466	0.483	0.527	0.568

The Q-test:

Compare the value of Q_{exp} from the equation above to the critical value of $Q_{critical}$.

- If $Q_{exp} \geq Q_{critical}$ then the suspect value can be rejected.
- If $Q_{exp} \leq Q_{critical}$,the value should be retained in the data set.

For additional information consult Rorabacher, D. B. "Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's 'Q' Parameter and Related Subrange Ratios at the 95% confidence Level," *Anal. Chem.* **1991**, *63*, 139–146. (see also http://chem-net.blogspot.com/2013/01...atistical.html)

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14.1.4.6: Guidelines for Recording and Reporting Data in your ELN

Always consider uncertainty during an experiment, record it in your ELN, and include it in all calculations and reporting. Do not leave the lab until you are sure that you have a valid strategy for determining errors in all final values.

1. **Uncertainty Awareness:**
   Before leaving the lab area, ensure you have a valid strategy for estimating uncertainties in all measured and calculated values.

2. **Estimating Uncertainty During Measurements:**

   - **Equipment Uncertainty**: Record uncertainties provided by equipment or manufacturers (e.g., balance deviation, pipette error). If unavailable, assume uncertainty is ±0.5 of the smallest measurable unit.
   - **Replicates**: For three or more measurements, calculate the standard deviation of the mean.
   - **Function-Based Values**: Perform propagation of error analysis.
   - **Least Squares Fitting**: Use errors from fitted parameters (e.g., slope or intercept) and propagate uncertainty if used in further calculations. Avoid linear regression if data deviates significantly from linearity.
   - **Consult Instructors**: Seek help for unclear sources of uncertainty.

3. **Propagation of Error:**
   Combine individual uncertainties to estimate the overall uncertainty of the final result. Use partial derivatives where necessary, and assume constants (e.g., RR) are error-free.

4. **Reporting Results:**

   - Include propagated uncertainty with each result.
   - Compare results with literature values using percent or absolute error.
   - Ensure significant figures reflect uncertainty and justify their use.

5. **Replicate Measurements:**

   - Report the mean and precision (e.g., standard deviation).
   - Use the Q-test to justify excluding outliers.

6. **Single Measurements:**

   - Estimate and report uncertainty (random or systematic).
   - Compare accuracy to expected values if available.

7. **Least Squares Fitting:**

   - Use weighted or non-weighted regression based on data.
   - Reject outliers only using the Q-test on residuals.
   - Propagate uncertainty from fitted parameters to calculated values.

8. **Qualitative Uncertainty:**

For variables with no clear quantitative uncertainty, discuss potential sources and their impact on results. Provide reasonable estimates and substantiate with evidence.

9. **Before Leaving the Lab:**
    - Confirm all uncertainties are documented.
    - Check for systematic errors (e.g., calibration issues).
    - Ensure thorough records of measured values and associated uncertainties.

By following these steps, you ensure your experimental results are accurate, reproducible, and clearly reported.

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14.1.4.7: Homework Problems

📅 **Pre-lab Due**: Attempt all seven problems before 1 pm on the scheduled meeting on this topic (see syllabus agenda). Your pre-lab assignment will be graded based on evidence of sincere effort, and work shown, but not on accuracy.

📅 **Final Problem Set Due**: The final problem set is due at 1 pm one week after our scheduled meeting on this topic (see syllabus agenda). The final problem set will graded based on work shown, thorough and accurate responses to questions, accuracy of calculation, and correct reporting (including units).

🎯 **Purpose:** Learn how to correctly estimate experimental uncertainty, and how to correctly report a value and its estimated uncertainty. This practice will get you ready to perform uncertainty analysis for your own experimental measurements this semester (and in the future).

Each practice problem below requires that you correctly apply either **statistical analysis** or **propagation of uncertainty** to estimate the uncertainty in a calculated value. Each problem also asks you to correctly report calculated values and their uncertainties.

Uncertainty analysis

This is the expected workflow for analysis of experimental values in P-Chem Lab:

Calculate → estimate uncertainty → report value ± uncertainty appropriately → justify the reporting → interpret what the uncertainty tells you.

Python (using Jupyter Notebooks in CoLab) is the recommended tool for completing this problem set. However, you may complete this assignment using any tool including pencil and paper, excel, etc. **You must understand the work you do, thus you may not use AI to complete this assignment.**

After submitting your initial attempts before the meeting, you will work with other students during our meeting to reach consensus about the strategies used to answer each question, and how to report each value and its uncertainty. Your instructors will be with you to answer your questions and to help guide your discussions. After the meeting, you will submit your revised work and final answers.

Your answers to these problems may be hand-written or typed. However, any submissions that are deemed illegible, unclear, or poorly organized will not be accepted.

Note

(1) We recommend that you use python to complete this problem set – we have provided some CoLab notebooks to help guide you. However, you may use whatever technology (calculators, software, etc.) you like to aid in working these problems.

(2) No matter what tools you use, it is important to show how your calculations are set-up and, where appropriate, give a sample calculation. Simply giving the final answer is not acceptable.

(3) In reporting all results, you should always round your reported answer to be consistent with your estimated uncertainty. For example: a calculated result of 56.2189 ± 0.0386 would be reported as **56.20 ± 0.04** where 0.04 is the standard deviation or propagated uncertainty. *See reading assignments for details about reporting*.

The seven problems are below. Note that there are custom CoLab tutorials to help you through this problem set. See Canvas and/or your Google Classroom to find the tutorials.

PROBLEM 1: Estimate Uncertainty using Statistics

A student makes five independent measurements of each of the linear dimensions of a box. The results are tabulated as follows:

Measurement	Length (cm)	Width (cm)	Height (cm)
1	1.010	5.376	2.001
2	1.015	5.339	2.105
3	1.013	5.385	1.985
4	0.999	5.375	1.989
5	1.009	5.369	2.008

A. **Summarize the measurements:** calculate the mean ($\bar{x}$), sample standard deviation (s), and relative standard deviation ($\%RSD = \frac{s}{\bar{x}} \times 100$). Report $\bar{x} \pm s$, and $\%RSD$ for each dimension (length, width, height) using appropriate units and appropriate precision.

B. **Compare the precision of the measurements**: Which dimension was most precise? ...least precise? Explain what statistical parameters from calculations in (A) are the most appropriate for comparing the precision of measurements that have different magnitudes. Support your answers using calculated values from (A).

C. **Calculate the volume**: Each row of the table represents one set of independent measurements of the box.
   - Calculate volume for each trial. This should produce five calculated volumes from the independent measurements of length, width, and height.
   - Then calculate the mean ($\bar{x}$), sample standard deviation (s), and relative standard deviation ($\%RSD$).
   - Report $\bar{x} \pm s$, and $\%RSD$ for volume using appropriate units and appropriate precision.

D. **Interpret results and justify choices for reporting:** Write a short paragraph that addresses the following points.
   - Which measurement (length, width, height) contributes the greatest uncertainty to the calculated volume?
   - Does the calculated volume appear to be more or less precise that the individual measurements? Explain, using evidence from your calcuations to support your argument.
   - Justify your choices in reporting to appropriate precision; in other words, what justifies "appropriate precision" of these values.

PROBLEM 2: A Simple Case for Propogation of Uncertainty

A student weighs a sample using an analytical balance, with an estimated uncertainty of ±0.5 mg in each measurement. Using the data below, determine the mass of the sample and the propagated uncertainty in that mass.

Item measured	Mass (g)
Sample and flask	5.1647 ± 0.0005
Empty flask (tare)	2.3712 ± 0.0005

A. Calculate the mass of the sample.
B. Calculate the propagated uncertainty in the sample mass.
C. Report the sample mass $\pm$ uncertainty: report using appropriate units and precision.
D. Explain why the propagated uncertainty is larger than the uncertainty in either individual mass measurement.
E. Justify the number of decimal places used in your final reported answer.

PROBLEM 3: Statistics and Rejection of Discordant Data

An investigator measures photon emission from the reaction shown below. The emitted photons (at 589 nm) are detected using a photomultiplier. For each run, the investigator measures both the total counts (signal + background) and the background counts.

$$Na^+ + O^- \rightarrow Na^* + O \overset{h\nu}{\rightarrow} Na + O$$

Run #	**Signal + Background (counts/sec)**	**Background (counts/sec)**
1	1500	1000
2	1200	1250
3	1375	1100
4	1425	900
5	1280	1200
6	1490	1363

The signal of interest is obtained by subtracting the background from the signal + background measurement.

A. **Determine the signal for each run.** Examine the resulting values before doing any further calculations. What do you notice about the data?
B. **Calculate the mean and standard deviation of the signal measurements.** Your software will probably display more digits than are meaningful. **Do not simply copy the numbers produced by the computer.** Decide how the mean and standard deviation should be reported, and explain your reasoning.
C. **One or more of these measurements might look suspicious.** Should any measurement be removed simply because it looks unusual? Explain briefly.
D. **Use the Q-test at the 90% confidence level to determine whether there is statistical justification for rejecting the suspicious measurement(s) as discordant.** Clearly identify the value(s) you test and compare Q_{calc} with Q_{crit}.
E. **Based on your statistical analysis, report your best estimate of the signal and its uncertainty.** Explain what the standard deviation tells you about the precision of this measurement, and is the standard deviation sufficient for estimating uncertainty? What other ideas might guide your decision for how to report the final value?

PROBLEM 4: Least Squares Analysis and Rejection of Discordant Data

The following experimental data are expected to show an approximately linear relationship between x and y.

Data Point	1	2	3	4	5	6	7
x	26	30	44	50	62	68	74
y	92	85	78	81	54	51	40

Your goal is to determine whether a linear model reasonably describes these data and to investigate whether there is statistical justification for rejecting any observation as an outlier.

A. **Plot and examine the data:** Create a scatterplot of y versus x. Before performing a regression, describe what you see.
   - Does a linear relationship appear reasonable?
   - Is the relationship positive or negative?
   - Does any point look unusual? If so, identify it.

B. **Fit a linear model:** Perform a linear least-squares regression and determine the slope, intercept, and correlation coefficient, r.
   - Add the best-fit line to your plot.
   - Report the equation of the fitted line on the plot, using an appropriate number of digits.
   - Report both the value and uncertainty for the slope and intercept. Justify your choices in reporting to appropriate precision; in other words, what justifies "appropriate precision" of these values.
   - Then interpret your result:
     - What does the **sign** of the correlation coefficient (r) tell you?
     - What does the **magnitude** of r tell you?
     - Does a large value of $|r|$, by itself, demonstrate that every observation is well described by the model? Explain.

C. **Examine the residuals:** For each observation, calculate the y-residual from the equation below (14.1.4.7.1) and create a plot of residual versus x.

$$\text{residual} = y_i - y_{predicted,i} \tag{14.1.4.7.1}$$

   - If the linear model adequately describes the data, what would you expect the residuals to look like?
   - Examine your residual plot. Do you see evidence of a systematic pattern, or does one observation appear particularly unusual? Identify the observation you would investigate further and explain your choice.

D. **Test the suspicious data point:** A point that looks unusual should not be discarded simply because removing it might improve the fit. Apply the **Q-test to the y-residuals** to determine whether there is statistical justification for rejecting the questionable observation. Compare Q_{expt} with the appropriate Q_{crit} at the **90% confidence level**. Based on this comparison, is there statistical justification for rejecting the observation? Explain your decision.

E. **What happens if the point is removed?** Regardless of your decision in Part D, temporarily remove the questionable observation and repeat the linear regression (Parts A, B, C above). This is an exploration, not permission to discard the measurement. Compare the regression **with and without** the suspicious data point. Consider slope, intercept, correlation coefficient r, and residuals.

F. **Make a scientific argument.** Did removing the questionable point substantially change the relationship between x and y? Support your conclusion with quantitative evidence from the two regression analyses.

PROBLEM 5: Propagation of Uncertainty

In a chemistry lab, students obtain the following data and are asked to find the **molecular weight (MW) of methanol** using the

ideal gas law, $PV = nRT$.

	Pressure (methanol)	Temperature	Mass (of methanol)	Volume
Trial 1	72.5 ± 0.5 mm Hg	295.10 ± 0.05 K	0.1331 ± 0.0002 g	1.05678 ± 0.00005 L
Trial 2	72.0 ± 0.5 mm Hg	295.05 ± 0.05 K	0.1329 ± 0.0002 g	1.05678 ± 0.00005 L

A. **Develop the function and determine MW**. Use the ideal gas law and the measured quantities to write a single expression for the molecular weight of methanol in grams per mole. Then calculate the molecular weight independently for each trial. ***Reminder**: pay attention to units, and perform unit conversions as necessary.*
B. **Propagate the uncertainty**. Determine the uncertainty in the molecular weight calculated for each trial. Clearly identify the uncertainty associated with each measured quantity and show how those uncertainties enter your calculation.
C. **Analyze the sources of uncertainty.** Which measured quantity contributes most strongly to the uncertainty in the calculated molecular weight? Support your answer quantitatively.
D. **Determine the average molecular weight and its uncertainty.** Calculate the average molecular weight determined from the two independent trials. Treat the two molecular wights as independently measured quantities and propagate their uncertainties through the calculation of the average. Report the average molecular weight and its uncertainty using appropriate units and precision.
E. **Justify your choices in reporting**. Explain how you determined the appropriate precision for the reported average molecular weight and its uncertainty.

PROBLEM 6: Propagation of Uncertainty

The Arrhenius relationship allows us to determine the activation energy for a reaction by measuring the rate constant at two different temperatures, according to the following expression.

$$ln\left(\frac{k_2}{k_1}\right) = -\frac{E_{act}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{14.1.4.7.2}$$

The rate constants for the reaction below was measured at two temperatures.

$$2DI \rightarrow D_2 + I_2$$

$k_{660} = (1.2 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $660 \pm 2K$

$k_{720} = (1.8 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $720 \pm 2K$

A. **Develop the function and determine the activation energy**. Use the Arrhenius expression (eq. 14.1.4.7.2) to develop a function for calculation of E_{act}. Then use the two independent measurements of k and T to calculate the E_{act}.
B. **Propagate the uncertainty in E_{act}.** Develop the function for calculation of uncertainty and determine the uncertainty in the value of E_{act}.
C. **Report and interpret the results.** Report E_{act} and its uncertainty using appropriate units and precision. Justify your choices in reporting.
D. **Analyze the sources of uncertainty.** Compare the contributions from k_1, k_2, T_1, and T_2. Which measurement(s) have the greatest influence on the uncertainty in E_{act}? Support your answer quantitatively.

PROBLEM 7: Propagation of Uncertainty

In the method of Clement and Desormes, the heat capacity (C) ratio of an ideal gas is determined from the manometrically determined values of P_1, the gas pressure at temperature T_1; P_2, the gas pressure immediately after a reversible adiabatic expansion when the temperature is T_2; and, P_3, the gas pressure after the gas has warmed back up to temperature T_1. The relationship used to calculate the heat capacity ratio is given by equation 14.1.4.7.3.

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{C_V}{R} + 1}{\frac{C_V}{R}} \tag{14.1.4.7.3}$$

where

$$\frac{C_V}{R} = \frac{P_2\left[1 - \left(\frac{P_3}{P_1}\right)\right]}{P_3 - P_2} \tag{14.1.4.7.4}$$

The following pressure data were collected:
P_1 = 763.1 ± 0.2 mmHg
P_2 = 757.0 ± 0.1 mmHg
P_3 = 758.7 ± 0.2 mmHg

A. **Develop the function and determine the heat capacity ratio, γ.** Use the equations above (eqs. 14.1.4.7.3 and \{refCD2}) to develop a function to calculate γ from the three pressure readings given above. Then use the function to calculate the value of γ.
B. **Propagate the uncertainty in each measured pressure to determine uncertainty in γ.** Calculate the uncertainty in the heat capacity ratio, γ.
C. **Report and interpret the result.** Report γ and its uncertainty with appropriate precision and units, if applicable. Justify your choices in reporting. Based on your uncertainty analysis, what can you conclude about the precision with which this experiment determines γ?

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14.1.4.8: References and Additional Reading

1. Shoemaker, D.P.; Garland, C.W.; Nibler, J.W. Experiments in Physical Chemistry, 6th Edition, McGraw-Hill, New York, NY, 1996, pp 27-89.

2. Bettelheim, F. A., Experimental Physical Chemistry, W.B. Saunders Co., Philadelphia, 1971, Chapter 2.

3. Brownlee, K. A., Statistical Theory and Methodology in Science and Engineering, 2nd Edition, John Wiley and Sons, Inc., New York, New York, 1965, pp 334-338.

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14.1.5: ABSORPTION SPECTRUM OF CONJUGATED DYES

You will measure the absorption spectra of a series of conjugated dyes and then use two theoretical models, the Particle-In-A-Box Approximation and, later, the Hückel Molecular Orbital Approximation to explain the observed spectra.

The general approach to this experiment is adapted from D. P. Shoemaker, C. W. Garland, and J. W. Nibler, Experiments in Physical Chemistry, 6th edition, McGraw Hill Co. Inc, NY, 1996, p378. The experiment has been revised to suit our laboratory environment.

14.1.5.1: Prelaboratory Assignment

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14.1.5.1: Prelaboratory Assignment

📅 **Due:** This assignment must be completed before 1:00 PM on your scheduled lab meeting day (see syllabus schedule).

🕒 **Time:** Plan at least two hours to complete this assignment.

🎯 **Purpose**: This pre-meeting assignment is designed to help you arrive to the meeting prepared to engage in thoughtful discussion and to conduct the experimental work.

This module includes **Wet Lab** work, thus you should prepare for your meeting by dressing appropriately for lab and bringing your own safety eyewear. In addition, for this and all following meetings, there is a written pre-lab assignment as described below. Because all experimental modules require similar preparation, the pre-lab assignment is divided into a "General" assignment that should be completed for each module and a "Specific" assignment for each meeting.

GENERAL Pre-Lab Assignment

A template file for preparing your pre-lab assignment is available in your Google Classroom Assignments.

Read the module in canvas and in the lab manual, follow the instructions within, then write a brief **introduction** to the experiment and an **experimental plan** using the following outline:

I. **Description of the Experiment:** In your own words, briefly introduce the topic, describe the theory upon which the experiment is based, and state the goals for this experiment. Keep it concise; lengthy discussions or derivations of equations are unnecessary.
   a. Background (importance/relevance): A brief description and justification of the importance of the topic, *with at least two references to source material* (do not use the lab manual as a reference). Describe the topic, and describe why is it interesting, important, and worth your time to learn.
   b. Theory: A concise paragraph or more describing the general theory for the method/technique used; this section should contain a reference to the appropriate pages of the textbook, or other source material from the literature.
   c. Goals/Purpose: Brief statement of purpose, which should indicate what is analyzed and the technique used. Limit to three to five sentences.

II. **Experimental Plan:** a short summary of the specific things that you would need to know in order to do the experiment without having access to your lab manual, with the understanding that you will always have a TA available to teach you how to use the instrument.

    The best way to approach this task is to thoroughly read the procedure for the experiment. While reading, take notes on the specifics of the work. What chemicals will you use? If you have to make solutions, what solutions do you need to make and of what concentration? How will you prepare them? What instrument will you use, and what specific instrument settings will you need to input (sometimes you will find this information in the Appendices that discuss the use of the instruments)? How many runs of each sample will you do; and over what wavelength, or temperature, etc. range? You do not need to write down how to use the instrument; we will teach you that. Bottom Line: we want you to write down only that pertinent information about samples, sample preparation, instrument and instrument parameters, numbers of runs, and other things, that you will need to know in order to do your work.

In addition to the general pre-lab assignment, please complete the specific tasks listed below. Your assignment must be submitted on Canvas before the deadline.

SPECIFIC Pre-Lab assignment for Absorption Spectra of Conjugated Dyes

1. Complete the general pre-lab assignment.

2. **Find structures for the four dyes to be studied in this experiment.** This information is readily available on the Sigma-Aldrich web site (http://www.sigmaaldrich.com) by searching for the name of each dye. Use ChemDraw to create a figure that shows the full chemical name, abbreviated name (Dye 1, etc), and the skeletal structure of each dye. It is unnecessary to include the counterion (iodide or chloride) in your stuructures. Include this figure in your pre-lab assignment.
   - **Dye #1**: 1,1'-diethyl-2,2'-cyanine iodide
   - **Dye #2**: 1,1'-diethyl-2,2'-carbocyanine chloride
   - **Dye #3**: 1,1'-diethyl-2,2'-dicarbocyanine iodide
   - **Dye #4**: 1,1'-diethyl-4-4'-carbocyanine iodide
3. **Use your knowledge of HOMO and LUMO to answer the questions below.**
   a. Give a definition of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).
   b. How are HOMO and LUMO related to UV-Vis absorption spectroscopy, specifically in the context of the λ_{max} values of these dyes?
   c. How does the HOMO-LUMO energy gap change as the length of a conjugated π system increases? (consider your knowledge from organic chemistry)
4. Examine the **structure** of each dye (specifically the length of the conjugated chain between the N atoms).
   - Compare and contrast the structures of the four dyes.
   - Based on the **particle in a box model** ($\Delta E = \frac{(N+1)h^2}{8mL^2}$) , where L is the length of the box, what trend do you expect in the λ_{max} values of this series of dyes? Justify your prediction.
5. Using your knowledge of **Beer's Law**, draw absorbance spectra in the range of 400 - 800 nm (example blank plot axes provided below).
   a. On plot A and B, sketch the spectrum of a dye molecule that absorbs light with $\lambda_{max} = 700$ nm at absorbance of 0.8 A.U.
   b. On plot A, add the spectrum of the same dye at half of the original concentration.
   c. On plot B, add the spectrum of a second dye that has $\lambda_{max} = 500nm$.
   d. On plot B, in a separate color or line thickness, show the spectrum that would occur if the two original dye solutions were mixed together in equal portions.
   e. Provide a concise justification of your predicted spectra; specifically justify your prediction for how the spectrum changes upon dilution (plot A) and how the spectrum changes upon mixing (plot B).

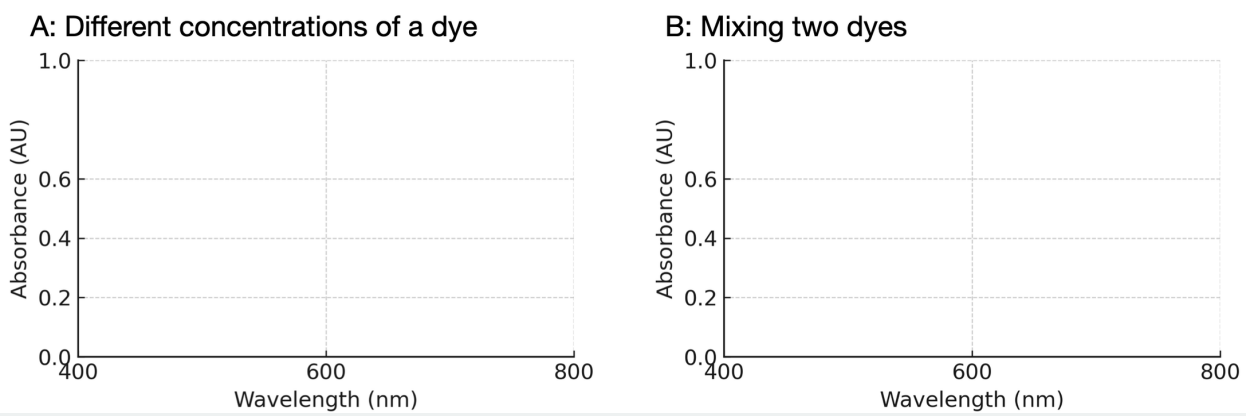


Figure 14.1.5.1.1: Predicted Absorption Spectra of Dyes. A) Shows a Dye with $\lambda_{max} = 700$ at two different concentrations. B) Shows predicted spectra of two dyes before and after mixing. (CC-BY-NC-SA; Kathryn Haas 2025)

6. Read one of the following (Duke students click here):
   - Change, R., Physical Chemistry for the Chemical Sciences, University Science Books, CA, 2014 (Section 10.9)
   - Chang, R., Physical Chemistry for the Chemical and Biological Sciences, University Science Books, CA, 2000 (Section 14.8)

Additional reminders

Since this is the first time you will be going into lab, we recommend reviewing the Chemistry Department Safety Manual and the Orientation Module. Here are some critical reminders:

- **Wear Protective Clothing**: As always, please dress appropriately for a laboratory environment. You will not be permitted to

enter lab, and thus will lose the opportunity to participate in the course assignments, if you fail to dress appropriately.

- **Prepare by completing the Pre-Lab Assignment**: It is absolutely essential that each student be prepared for lab meetings by reading the appropriate module in this manual, and by completing the specified pre-laboratory assignments. The pre-lab assignment must be submitted as a single pdf document on Canvas before the scheduled lab meeting. The pre-laboratory assignments are designed to prepare you to operate efficiently and safely during the experimental module. You will not be allowed to conduct experiments if the pre-lab assignment is not completed before your lab meeting. If there is an extenuating circumstance that prevents your preparation, please inform your instructors as soon as possible.
- Your preparedness will be evaluated by the quality of your work on pre-lab assignments, your answers to oral questions pertaining to the laboratory from the instructors, and/or your responses to unannounced quizzes and skills checks.

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14.1.6: ROTATION-VIBRATION SPECTRUM OF HCL

14.1.6.1: Pre-lab Assignment

14.1.6.2: Background on Rotovibrational Spectroscopy

14.1.6.2.1: The Electromagnetic Spectrum and Molecular Transitions

14.1.6.2.2: Rotational Transitions Accompany Vibrational Transitions

14.1.6.2.3: Transition Intensities

14.1.6.2.4: The Pure Rotational Spectrum has Unequal Spacings

14.1.6.2.5: Anharmonicity and Vibrational Overtones

14.1.6.3: Experimental and Instructions

14.1.6.4: References

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14.1.6.1: Pre-lab Assignment

📅 **Due:** Each part of this assignment must be completed before 1:00 PM on each scheduled lab meeting day (see syllabus schedule).

- **Part I is due prior to the first week's Wet Lab meeting (see syllabus agenda).**
- **Part II is due prior to the second week's Wet Lab meeting (see syllabus agenda).**

🕒 **Time:** Plan at least two hours to complete this assignment each week.

🎯 **Purpose**: These pre-meeting assignments are designed to help you arrive to each week's meeting prepared to engage in thoughtful discussion and to conduct the experimental work.

This module has two parts and is usually completed over two laboratory meetings. Each meeting includes **Wet Lab** work, thus you should prepare for both meetings by dressing appropriately for lab and bringing your own safety eyewear. Wear PPE and gloves when handling hazardous materials.

For both meetings, there is a written pre-lab assignment as described below. Complete the **GENERAL PRE-LAB ASSIGNMENT** for both meetings as well as the specific assignment for each meeting. Part I corresponds to the first meeting, and Part II corresponse to the second meeting.

Specific Pre-Lab Assignment for Part I: *What can FTIR tell us about a molecule?*

📅 **Due before Meeting 1**

Read sections 5.1 through 5.3 of this manual and complete the GENERAL PRE-LAB ASSIGNMENT for this part of the module. Then complete the following written assignment and submit your work before the deadline.

1. Consider the types of molecular motions and their energies:
   a. What types of motion can gas-phase molecules exhibit?
   b. In general, what type of motion allows molecules to absorb infrared radiation?

2. The frequency of electromagnetic radiation is often reported in units of wavenumbers (cm^{-1}). Consider the equation $E = \frac{hc}{\lambda}$ and to determine whether wavenumbers (use units as your guide) are directly or inversely proportional to energy.

3. Consider a hypothetical diatomic gas with a typical harmonic frequency of 2000 cm^{-1}.
   a. *Apply the Harmonic Oscillator Model*: Draw the energy level diagram corresponding to the vibrational energy levels for this molecule (assume an ideal harmonic oscillator).
   b. *Energies of Molecular Motion*: To which region of the electromagnetic spectrum do transitions between these energy levels belong?
   c. *Predict a spectrum*: A sample of this diatomic gas is placed in a spectrometer capable of measuring absorbance in the range 1000 – 5000 cm-1. Predict the appearance of the spectrum (intensity of absorbance vs. frequency). Put frequency (in cm^{-1}) on the x-axis and intensity of absorbance on the y-axis. Draw the spectrum and explain you reasoning.
   d. *Link your prediction to the model*: Go back to the energy level diagram you drew in 3A. Add an arrow to your energy level diagram from 3A to represent each transition drawn in your spectrum in 3C.

Specific Pre-Lab Assignment for Part II: *How does the instrument resolution affect the results?*

📅 **Due before Meeting 2**

Review the group discussion guide worksheets that you completed during the first meeting, the data you collected, and your data analysis. Read section 5.4 of this module and complete the GENERAL PRE-LAB ASSIGNMENT for this part of the module, and the items below.

4. Find the rotovibrational models that you derived and fit to the experimental data in the previous meeting. Write the expression for each. Then define each one of the parameters (with units).
5. Describe how you can identify each of the parameters' values from theory or calculate it using the experimental data you collected.
   - m
   - $\tilde{\nu}$
   - α
   - $\tilde{B}$
   - $\tilde{D}$
   - Moment of Inertia (I_e)
   - Equilibrium bond length (r_e)
6. Show the equations by which you would find uncertainty in each parameter using the results of nonlinear fitting ($\Delta\tilde{\nu}$, $\Delta\alpha,;\ \Delta\tilde{B},\ \Delta\tilde{D},;\ \Delta I_e,\ \Delta r_e$).
7. *Predict the effect of resolution*: What will happen to the FTIR spectrum and the derived molecular parameters as instrument resolution is changed from 8 cm^{-1} to 0.5 cm^{-1}? Show your prediction by sketching the spectrum for at least three different resolutions. Describe the trend you expect in the molecular parameters as resolution is varied.

Adapted from Beck, Jordan P., and Diane M. Miller. “Encouraging Student Engagement by Using a POGIL Framework for a Gas-Phase IR Physical Chemistry Laboratory Experiment.” *Journal of Chemical Education* 99, no. 12 (December 13, 2022): 4079–84. https://doi.org/10.1021/acs.jchemed.2c00314.

Additional reading: (available in the library, Duke students click here)

- Part I. Instrumentation, *Journal of Chemical Education,* **1986,** *63* (1), A5. (This is a description of how the Michaelson Interferometer is applied in FTIR spectroscopy. See also the video lined below.)
- Shoemaker, D.P., Garland, C.W., and Nibler, J.W. Experiments in Physical Chemistry, 6th ed., McGraw-Hill, New York, 1996, Chapter XIV, **Experiment 37**.
- McQuarrie, D.A. and Simon, J.D. "Physical Chemistry: A Molecular Approach", University Science Books, CA, 1997, Sections 13.2-13.4, 18.4-18.5); Atkins, P., Physical Chemistry, 5th ed., sections 16.8 – 16.11
- Silbey, R.J., Alberty, R. A. Bawendi, M.G., Physical Chemistry, 4th ed., Sections 13.4, 13.6 and 13.7, for a discussion of rotation-vibration spectroscopy of diatomic molecules.

Optional videos

Dr. Welsher's P-Chem lectures are on YouTube!

In addition, the videos below provide a nice introduction and demonstration of the theory and techniques you will use.

Introduction to the Michaelson Interferometer in FTIR

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

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14.1.6.2: BACKGROUND ON ROTOVIBRATIONAL SPECTROSCOPY

A note from your instructors

We are working to replace the commercial textbooks used in this course. While we're still working on it, we are providing the following sections (which are still under construction). The section on transition intensities is the only section that was part of the original manual for this course, and is not covered in the Shoemaker textbook.

14.1.6.2.1: The Electromagnetic Spectrum and Molecular Transitions

14.1.6.2.2: Rotational Transitions Accompany Vibrational Transitions

14.1.6.2.3: Transition Intensities

14.1.6.2.4: The Pure Rotational Spectrum has Unequal Spacings

14.1.6.2.5: Anharmonicity and Vibrational Overtones

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14.1.6.2.1: The Electromagnetic Spectrum and Molecular Transitions

Electromagnetic radiation, or light, exhibits dual behavior as both waves and particles. Wave properties, such as refraction, best explain phenomena like light passing through different mediums. Conversely, particle behavior provides a more accurate description in certain scenarios, like absorption and emission. The nature of electromagnetic radiation remains unclear, with wave and particle models coexisting since the development of quantum mechanics in the early 20th century. Despite this ambiguity, these dual models effectively characterize electromagnetic radiation.

It consists of oscillating electric and magnetic fields that travel through space at a constant velocity. In a vacuum, the speed of light (c) is $2.99792 \times 10^8 \frac{m}{s}$. When passing through a medium other than a vacuum, its velocity (v) is slightly less than c, with the difference being <0.1%. For practical purposes, the speed of light is often approximated as $3.00 \times 10^8 \frac{m}{s}$. The oscillations in the electric and magnetic fields are perpendicular to each other and the wave's propagation direction. A model of plane-polarized electromagnetic radiation, featuring a single oscillating electric field and a single oscillating magnetic field, is illustrated in Figure 14.1.6.2.1.1.

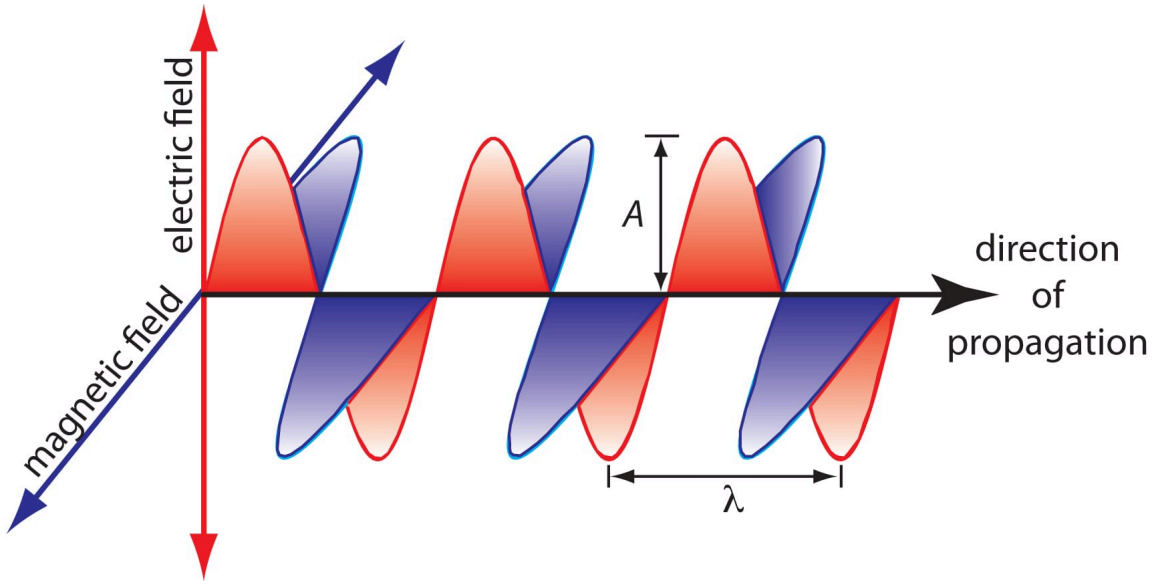


Figure 14.1.6.2.1.1: Plane-polarized electromagnetic radiation showing the oscillating electric field in **red** and the oscillating magnetic field in **blue**. The radiation's amplitude, *A*, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \phi) \tag{14.1.6.2.1.1}$$

where A_t is the magnitude of the electric field at time t, A_t is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at t = 0. The identical equation for the magnetic field is

$$A_t = A_m \sin(2\pi\nu t + \phi) \tag{14.1.6.2.1.2}$$

where A_m is the magnetic field's maximum amplitude.

Units of energy

The **wavelength**, λ, is defined as the distance between successive maxima (Figure 14.1.6.2.1.1). The relationship between wavelength (in m) and frequency (in s^{-1} or Hz) is given below. Wavelength is usually expressed in nanometers (1 nm = 10^{-9} m) for ultraviolet and visible light, and in microns (1 μm = 10^{-6} m) for infrared light.

$$\lambda = \frac{c}{\nu} \tag{14.1.6.2.1.3}$$

Wavelength is a unit used often by chemists, especially in UV-vis spectroscopy. Because it is inversely related to energy (ie smaller wavelengths are higher energy), many scientists prefer units that are directly proportional to energy. An alternate unit, the **wavenumber**, $\tilde{\nu}$, is used frequently, especially in infrared spectroscopy. In general it seems to be the preferred unit of physicist due to its direct correlation to energy. It is useful to know how to convert between these two commonly-used units. The unit $\tilde{\nu}$ is simply the reciprocal of wavelength.

$$\tilde{\nu} = \frac{1}{\lambda} \tag{14.1.6.2.1.4}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Keeping symbols straight

Heads up! The word "frequency" refers to cycles per unit time, but can also be measured in a length scale. Frequency measured in cycles per seconds (s^{-1} can be expressed in the metric base unit Hertz, and can have the symbol f or ν. When it is expressed in a length scale, like wavenumbers (cm^{-1}), it has the symbol $\tilde{\nu}$.

- When converting units from ν (in s^{-1}) to λ, use the speed of light to convert between time and length scales as in 14.1.6.2.1.3.
- When converting from $\tilde{\nu}$ to λ, use 14.1.6.2.1.4 and convert metric units as necessary.

Regions of the Spectrum and Types of Transitions

Electromagnetic radiation spans a wide range of frequencies and wavelengths, prompting the division of this spectrum into distinct regions for convenience, known as the **electromagnetic spectrum** (Figure 2). These divisions are based on the atomic or molecular transitions responsible for the absorption or emission of photons. It's important to note that the boundaries between these regions are not fixed, allowing for potential overlap between different spectral regions.

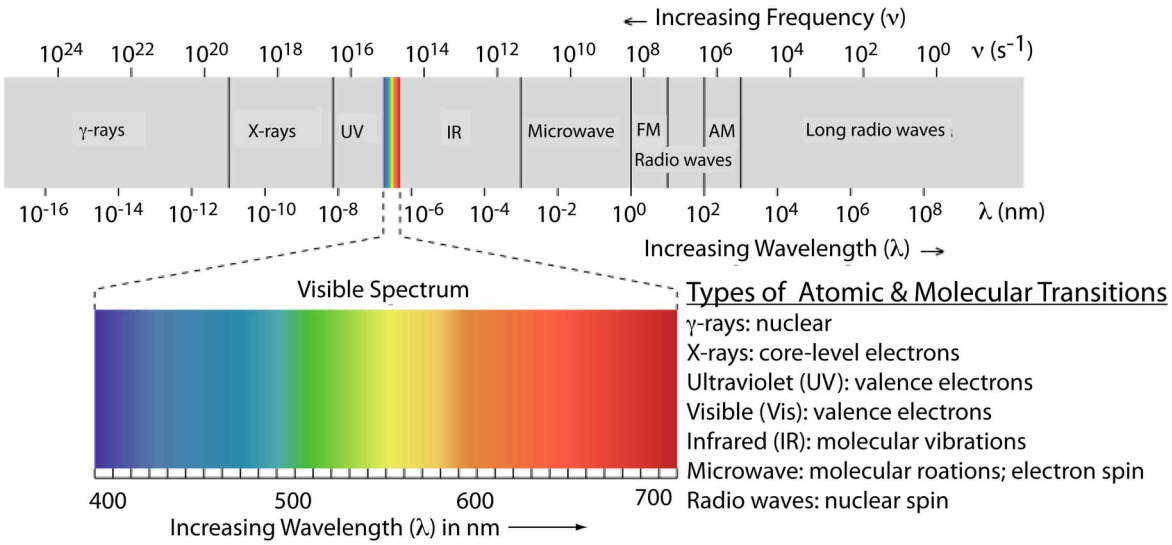


Figure 14.1.6.2.1.2: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

Given the energy levels of molecules and their corresponding wavelengths, we can determine the frequency within the electromagnetic spectrum regions using the equation:

$$\Delta E = E_u - E_l = h$$

Here, h represents the energy change between the upper (u) and lower (l) states.

The frequencies of molecular transitions fall within specific ranges. These ranges are listed in the table below in order of increasing energies.

Table 14.1.6.2.1.1*: Each type of molecular motion and its corresponding region of the electromagnetic spectrum. Ranges are approximate.*

Region	Wavelengths (nm)	Frequency (cm^{-1})	Frequency (s^{-1})	Transitions
Microwave	~10^9 - 10^6	~ 0.01 - 10	~10^8 - 10^{11}	**rotational transitions**
Infrared	~10^4 - 10^3	~200 - 4,000	~10^{12} - 10^{14}	**vibrational transitions**
Visible and Ultraviolet	~750 - 10	~ 13,300 - 1,000,000	~10^{14} - 10^{16}	**valence electronic transitions**

Contributors and Attributions

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- David Harvey (DePauw University)

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14.1.6.2.2: Rotational Transitions Accompany Vibrational Transitions

The infrared region (IR) of the electromagnetic spectrum is of interest to chemists because it corresponds to the energy of the vibrational modes of molecules (specifically the region between 4000 to 400 cm^{-1}). When the frequency of infrared radiation matches the vibrational frequency of a molecule, the molecule can become vibrationally excited by transitioning from the vibrational ground state to a vibrational excited state. In the case of diatomic molecules, like HCl, there is only one vibrational mode. Thus, we might expect one vibrational absorption band in the IR spectrum.

However, in the gas phase IR spectrum of HCl, there is a complex pattern of bands (see Figure 14.1.6.2.2.1). The structure that is observed in the IR spectrum of HCl was one of the early pieces of evidence supporting quantum mechanics and the idea that molecular states (like vibrational and rotational states) are quantized. The person who first measured a high-resolution spectrum like the one shown in Figure 14.1.6.2.2.1, and who used this spectrum as experimental confirmation of the Franck–Condon principle, was a **Elmer Imes** (click here for Wikipedia - unfortunately, we couldn't find a public domain photo of him, but google his name and you'll find him!). Imes is best known for his collaboration with James Franck in 1926, where they conducted experiments on molecular spectra (like Figure 14.1.6.2.2.1) and provided experimental confirmation of the Franck–Condon principle. This principle relates to the intensity distribution of vibrational transitions in molecular spectra. Imes was the first African American in the 20th century to gain a Ph.D., and he became a physics professor at Fisk University. Elmer Imes's work, along with that of his contemporaries, laid the foundation for our understanding of molecular structures and behaviors, particularly in the realm of rotational-vibrational spectroscopy. His contributions have had a lasting impact on the study of molecular physics and spectroscopy.

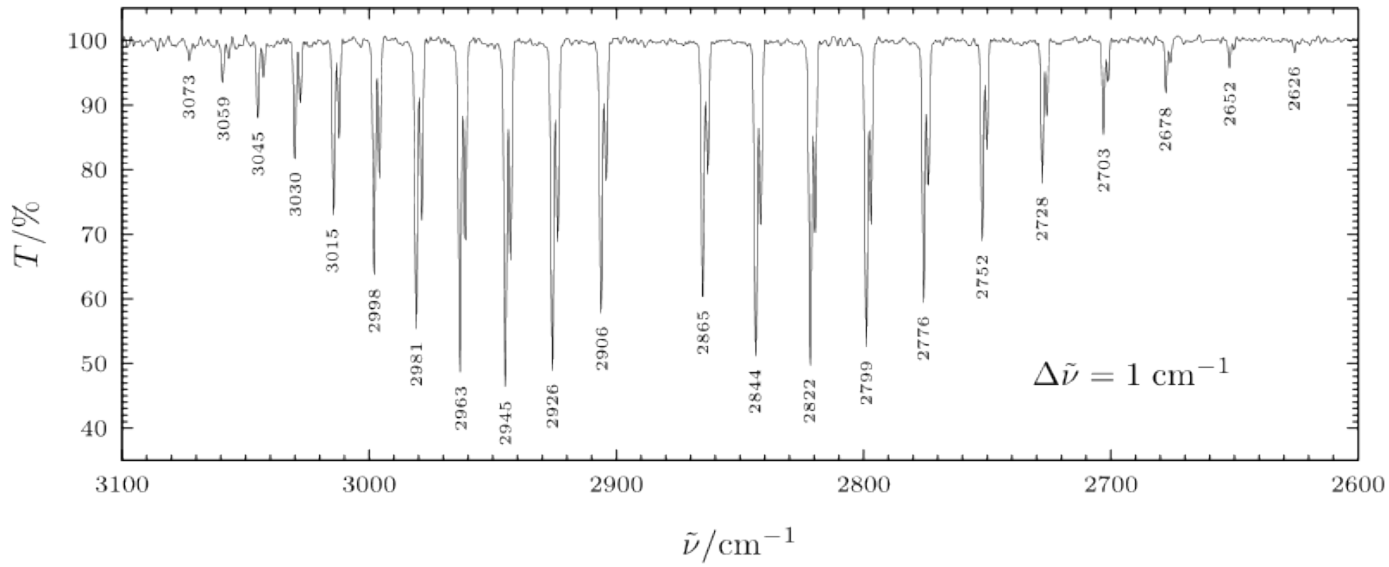


Figure 14.1.6.2.2.1. Gas phase FTIR spectrum of HCl. In this view, the data is plotted in a similar fashion as you may have seen in organic chemistry courses. The intensity is shown as % transmission on the Y axis and wavenumbers on the X axis. The X axis is plotted from high to low wavenumber. Figure used with permission from Wikipedia.

While every peak on the spectrum shown in Figure 14.1.6.2.2.1 represents a transition from the ground vibrational state to the first vibrational excited state, each represents a unique transition from one rotational state of the ground vibrational state to a different rotational state of the vibrational exited state. This coupling of rotational and vibrational states that appears in the IR spectrum in Figure 14.1.6.2.2.1 illustrates the quantized nature of molecular motions.

Models of Molecular Motion

To explain the spectrum shown above, we start by considering all the possible molecular motions and using simple models to describe them.

VIBRATIONAL motions and the HARMONIC OSCILLATOR model

The HCl molecule vibrates along the bond axis. We can treat the molecule's **vibrations** as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete energies given by

$$E(\upsilon) = h\nu\left(\upsilon + \frac{1}{2}\right) \text{ or } \tilde{E}(\upsilon) = \tilde{\nu}\left(\upsilon + \frac{1}{2}\right) \tag{14.1.6.2.2.1}$$

Where υ is the vibrational quantum number and can have integer values 0, 1, 2, 3...etc., and ν or $\tilde{\nu}$ is the frequency of the vibration given by:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}} \tag{14.1.6.2.2.2}$$

where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{14.1.6.2.2.3}$$

At room temperature, nearly 100% of the molecules are in their ground vibrational state $\upsilon = 0$ according to the Boltzman distribution. By convention, the ground vibrational state is indicated by a double prime (") while the exited state is indicated by a single prime (').

- **Ground state:** $\upsilon'' = 0$**, nearly homogeneous population in the ground state at room temp.**
- **First excited state:** $\upsilon' = 1$

At room temperature, the lowest energy vibrational state $\upsilon = 0$ is populated, so $\upsilon'' = 0$. Thus, the only reasonable transition is from $\upsilon'' = 0$ to $\upsilon' = 1$, and $\Delta\upsilon = +1$.

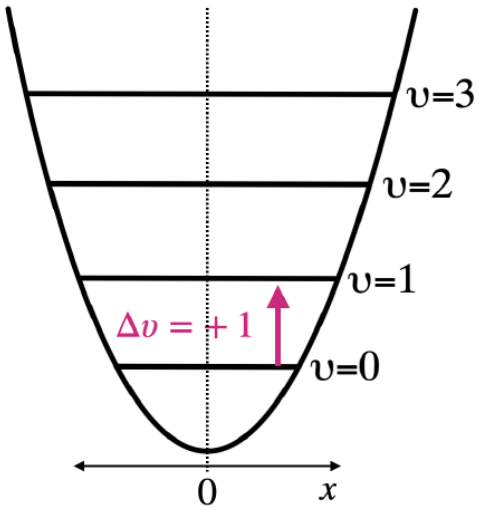


Figure 14.1.6.2.2.2: The potential energy (U) well of an 'ideal' harmonic oscillator. The well is defined by the function $U = \frac{1}{2}kx^2$, where k is the force constant and x is the displacement from equilibrium bond length. The vibrational quantum numbers (υ) are indicated for the first three vibrational energy levels. The transition between $\upsilon = 0$ to $\upsilon = 1$ is indicated by the magenta arrow. (Kathryn Haas; CC-BY-SA)

The harmonic oscillation is a useful approximation of a molecular vibration, but has key limitations:

- Due to equal spacing of the energy levels, all transitions would occur at the **same** frequency (i.e. you'd get a single line spectrum). However experimentally many lines are often observed (called overtones).
- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

"Real" bond vibrations are anharmonic

The vibrational energy levels of a real molecule are not evenly spaced and are more like that shown in the illustration in Figure 14.1.6.2.2.3, where the energies are more closely spaced as υ increases. However, the harmonic oscillator is a reasonable approximation at $\upsilon = 0$ and $\upsilon = 1$.

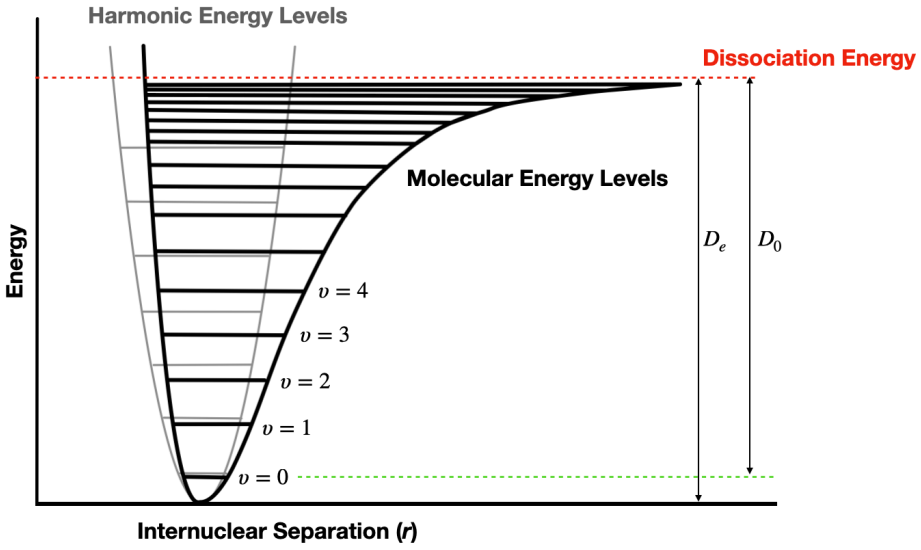


Figure 14.1.6.2.2.3: Illustration of vibrational energy levels predicted by the harmonic oscillator model and those of a real diatomic molecule. (Kathryn Haas; CC-BY-SA)

ROTATIONAL motions and the the RIGID ROTOR model

The HCl molecule also has rotational motions. We treat the molecule's **rotations** as those of a rigid rotor (ignoring centrifugal distortion from non-rigid rotor aspects). The energy of a rotation is also quantized in discrete levels given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \tag{14.1.6.2.2.4}$$

In which J is the rotational quantum number with integer values 0, 1, 2, 3...etc., and I is the moment of inertia, given by

$$I = \mu r^2 \tag{14.1.6.2.2.5}$$

where μ is the reduced mass (Equation 14.1.6.2.2.3) and r is the equilibrium bond length.

Experimentally, frequencies of light are measured (in units of cm^{-1}), so it is convinient to use these units in our expressions. The frequency can be divided by hc to give energy in units of wavenumbers. The expression for the rotational energy levels expressed in wavenumbers is $\tilde{E}_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 cI} J(J+1) = \tilde{B}J(J+1)$. And, we can simplify the expression by defining the rotational constant $\tilde{B}$ as

$$\tilde{B} = \frac{h}{8\pi^2 Ic} \tag{14.1.6.2.2.6}$$

This gives the allowed energies of rotation, in wavenumbers, as

$$\tilde{E}_J = \tilde{B}J(J+1) \tag{14.1.6.2.2.7}$$

Tip: It is important to note in which units you are working. The frequencies and rotational constants can have different units (eg Hz or wavenumbers). To keep track, we are using the tilde $\tilde{X}$ to indicate wavenumber units, but some texts don't do this - they always represent the rotational constant as B, whether in frequency or wavenumbers. Just be sure you are paying attention and are using consistent units in your calcaulations.

Just as in the notations for vibrational states, the convention for notating rotational ground state is by a double prime (") while the exited state is indicated by a single prime ('). The lowest-energy rotational state is $J'' = 0$. Rotational energy levels are very close in energy (much closer than vibrational energy levels), and so at temperatures close to room temperature, there is enough energy so that higher-energy states are populated (e.g. $J'' = 1, 2, 3...$ are also populated). The statistical probability of each rotational state being populated can be calculated using the Boltzmann distribution.

- **Ground state: J''; at room temperature there is heterogeneous population of the rotational states.**
- **Excited state: J'; upon excitation we can also expect a heterogenous population of excited states.**

The rotational energy states are closer in energy than vibrational energy states. And, real molecules undergo rotationas and vibrations simultaneously. Thus, one way to show the rotational energy levels is to superimpose them on a diagram of the harmonic oscillator vibrational energy levels, as is illustrated in Figure 14.1.6.2.2.3.

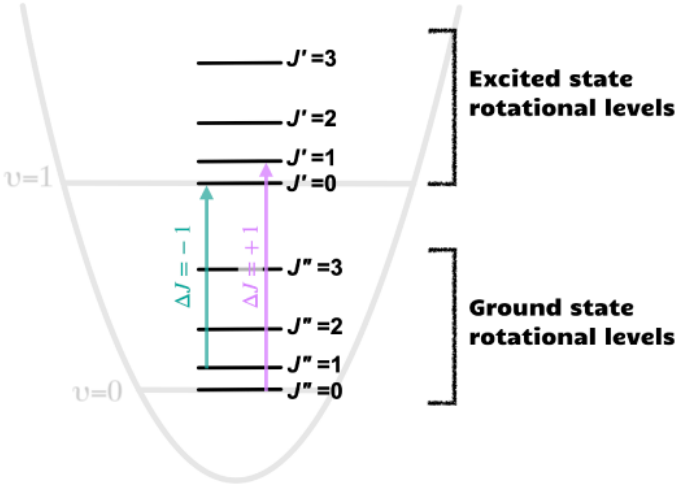


Figure 14.1.6.2.2.3: The rotational states are shown superimposed in the vibrational states. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels. All ground state rotational states are indicated by J'' in purple, and rotational states of the excited state are indicated by J' in orange. A transition with $\Delta J = +1$ is indicated by the arrow on the left. A transition with $\Delta J = -1$ is indicated by the arrow on the right. (Kathryn Haas; CC-BY-SA)

Combining rotational and vibrational models

Real molecules are rotating and vibrating simultaneously, and the rotational and vibrational states are coupled. We could express the energies of these motions (in wavenumbers) as a simple combination of rotational and vibrational motions:

$$\tilde{E}_{v,J} = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}_v J(J+1) \qquad (14.1.6.2.2.8)$$

However, this approximation ignores the fact that the rotational motions affect the centrifugal stretching of a bond, and thus the bond length and vibrational motions are afected by rotational motion. Vice versa, a vibrational excitation would increase the equilibrium bond length (r_e), and would affect the Moment of Inertia (I). A more complete representation of the energies of roto-vibrational states is expressed as a term value, $T(v, J)$, is given below. $T(v, J)$ in Equation 14.1.6.2.2.9 combines factors from rotational (rigid rotor) and vibrational (harmonic oscillator) energies, as well as factors that account for anharmonicity, centrifugal

stretching, and the interactions between rotational and vibrational motions.

$$T(\upsilon, J) = \frac{E(\upsilon, J)}{hc} = \tilde{\nu}_e \left(\upsilon + \frac{1}{2}\right) - \tilde{\nu}_e x_e \left(\upsilon + \frac{1}{2}\right)^2 + B_e J(J+1) - D_e J^2 (J+1)^2 - \alpha_e \left(\upsilon + \frac{1}{2}\right) J(J+1) \quad (14.1.6.2.2.9)$$

where c is the speed of light, $\tilde{\nu}$ is the frequency in cm-1, υ is the vibrational quantum number, J is the rotational quantum number, and r_e is the internuclear separation. This expression takes into account the following:

- Anharmonicity with the term $-\tilde{\nu} x_e \left(\upsilon + \frac{1}{2}\right)^2$, where $\tilde{\nu} x$ is the anharmonicity parameter in cm^{-1}.
- Centrifugal stretching with the term $-DJ^2(J+1)^2$, where D is a constant.
- The interaction between rotational and vibrational motions with the term $-\alpha \left(\upsilon + \frac{1}{2}\right) J(J+1)$ where α is the rotovibrational coupling constant that accounts for interactions between rotational and vibrational motions.

We can simply this through approximation of the harmonic oscillator by assuming that the the harmonic oscillator is good enough for the case where the vibrational transitions are occurring almost exclusively between the two lowest-energy vibrational states: $\upsilon'' = 0$ and $\upsilon' = 1$. This gives a reasonable approximation that we can use as a model for rotational and vibrational motions of a diatomic:

Approximate allowed energies of roto-vibrational states:

$$\tilde{E}_{\upsilon,J} = \tilde{\nu} \left(\upsilon + \frac{1}{2}\right) + \tilde{B} J(J+1) - \tilde{D}[J(J+1)]^2 - \tilde{\alpha} \left(\upsilon + \frac{1}{2}\right) J(J+1) \quad (14.1.6.2.2.10)$$

- $\tilde{E}$ is the energy
- $\tilde{\nu}$ is the vibrational frequency in cm^{-1}
- υ is the vibrational quantum number
- J is the rotational quantum number
- $\tilde{B}$ is the rotational constant
- $\tilde{D}$ is a constant related to centrifugal stretching
- $\tilde{\alpha}$ is the rotovibrational coupling constant in cm^{-1}

Selection Rules for vibrational and rotational transitions on diatomic molecules

- **Vibrational Transition Selection Rules**: The vibrational quantum number can change by 1: $\Delta\upsilon = \pm 1$. However, normally we can assume energy can only go upwards because of the nearly homogeneous population of $\upsilon'' = 0$ near room temperature.
- **Rotational Transition Selection Rules**: The rotational quantum number can change by 1: $\Delta J = \pm 1$. Since at room temperature, $J'' = 0, 1, 2...$ (several different rotational states are populated), transitions to higher and lower-energy rotational states are possible.

The P, Q, and R Branches

These selection rules mean that transitions with ΔJ or $\Delta\upsilon$ equal to 0, 2, 3...etc are not allowed. The fact that the transition $\Delta J = 0$ is forbidden means that a purely vibrational excitation (with no accompanying rotational transition) is not observed in the case of diatomic molecules. The rotational selection rule gives rise to distinct "branches" of the gas phase IR spectrum for diatomics like HCl; They are named using letters P, Q, R in order of increasing energy and corresponding to $\Delta J = -1, 0, +1$, respectively. Due to the unequal spacing of rotational energy levels, each transition requires a different energy.

At the highest energies are the transitions of the R-branch (when $\Delta J = +1$) and at the lowest energies are the transitions of the P-branch ($\Delta J = -1$). Between the P and R branches is the Q branch ($\Delta J = 0$). The Q branch is absent in the gas phase IR spectrum of HCl because $\Delta J = 0$ is forbidden; thus it appears as a gap in the spectrum . Figure $14.1.6.2.2.4$ illustrates allowed transitions on the energy diagram .

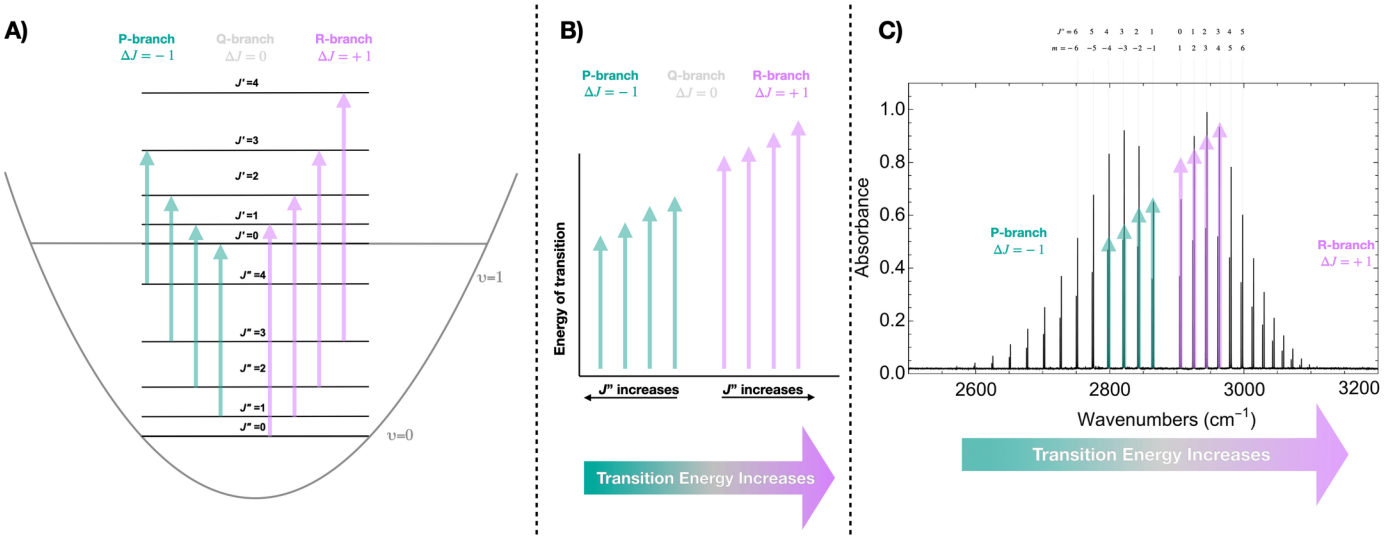


Figure 14.1.6.2.2.4: Allowed Rotation-Vibration Transitions are indicated using vertical arrows. The vibrational energy states are indicated with $upsilon$ and rotational energy levels indicated by J. **A)** The rotational energy levels (J) are superimposed on the vibrational energy levels of the ground state ($\upsilon\,''$) and first vibrational excited state (υ'). **B)** Illustration of the relative energy for transitions of P and R branches. Because of unequal spacing between the rotational energy levels, the individual transitions differ in energy. In **panel A**, arrows increase in magnitude from left to right. To illustrate this, each arrow from **panel A** is placed with tails aligned in **panel B** so their relative magnitudes are obvious. The magnitude of the energy transition is qualitatively indicated by the length of the arrow. C) The P and R branches, the m values, and the arrows from Panels A and B are annotated on the FTIR spectrum of HCl (taken at 0.1 cm^{-1} resolution). (Kathryn Haas; CC-BY-SA)

Frequencies of P, Q, and R Branches

The frequency of a rotovibrational transition is the difference in energy (in cm^{-1}) of the excited state and ground state: $T(\upsilon', J') - T(\upsilon\,'', J\,'')$. Thus the frequencies of vibrational transition from $v = 0 \rightarrow 1$ can be calculated from the Equation 14.1.6.2.2.9. The calculation is simplified by dropping D_e out of the equation, since D_e (the centrifugal distortion constant) is usually very small. Simplified equations for calculations of the frequencies of each peak in the R and P branches are given below.

R Branch frequencies

For peaks of the R-branch, where allowed J values are $J\,'' = 0, 1, 2, ...$ and $J' = 1, 2, 3...$, and $\Delta J = +1$, the vibrational frequency for a given $J\,''$ is:

$$\tilde{\nu}_R = \tilde{\nu}_0 + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)\, J'' - \alpha_e J''^2 \tag{14.1.6.2.2.11}$$

Q Branch (the forbidden frequency)

$$\tilde{\nu}_0 = \tilde{\nu_e} - 2\tilde{\nu_e} x_e \tag{14.1.6.2.2.12}$$

*this is the forbidden transition (because $\Delta J = 0$ is forbidden). This is the frequency of the forbidden "vibration-only" transition, and it appears as a gap in the spectrum.

P Branch frequencies

For peaks of the P branch, where allowed J values are $J\,'' = 1, 2, 3, ...$ and $J' = 0, 1, 2...$, and $\Delta J = -1$, the vibrational frequency for a given $J\,''$ is:

$$\tilde{\nu}_P = \tilde{\nu}_0 - (2B_e - 2\alpha_e)\, J'' - \alpha_e J''^2 \tag{14.1.6.2.2.13}$$

General equation for all frequencies

We can write a more general equation for the frequencies by defining a new value m, where $m = -J''$ for P branch, and $m = J''+1$ for R branch:

$$\tilde{\nu}(m) = \tilde{\nu}_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2 \tag{14.1.6.2.2.14}$$

Trends in peak spacing ($\Delta\tilde{v}$)

Consider a scenario where the interactions between vibrational and rotational motions is negligible, and thus α_e is small. In this scenario, the equations above (equations 14.1.6.2.2.11 and 14.1.6.2.2.13) would yield a linearly relationship between J'' and $\tilde{\nu}$. In this imaginary scenario, we would expect a spectrum with equally-spaced lines in the P and R branches, where the separation between the lines is $2B_e$ (in other words $\Delta\tilde{\nu} = 2B_e$).

However, in a real diatomic like HCl, there is significant interaction between vibrational and rotational motions, and α_e is significant. The result is a non-linear relationship between J' and $\tilde{\nu}$, where the spacing of the R branch decreases as J'' increases (R branch lines become more closely spaced), and the spacing in the P branch becomes larger as J'' increases (P branch lines become are farther apart).

R Branch peaks become more closely spaced

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{14.1.6.2.2.15}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value for increasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$ +(smaller and smaller value) as J increase. Because the rotational frequencies keep getting smaller, the spacing between lines in R branch decreases as J increases.

Increasing in Spacing of Lines in the P Branch with Decreasing J

Using the same analysis as above,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{14.1.6.2.2.16}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value even for decreasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$ −(smaller and smaller value) as J decreases. Because the rotational frequencies keep getting larger, the spacing between lines in P branch increase as J decreases.

References

1. McQuarrie, Donald A. Quantum Chemistry. New York: University Science Books, 2007.

Contributors and Attributions

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- Kathryn Haas

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14.1.6.2.3: Transition Intensities

Transition Intensities

The relative intensity of the P- and R-branch lines depends on the thermal distribution of rotational states; more specifically, they depend on the population of the J'' states. The intensity of a spectral line depends not only on the transition probability (selection rules) and the frequency ν (energy of radiation), but also on the number of molecules in any initial state. Since most infrared (IR) spectra are observed under conditions of thermal equilibrium, we need only consider the distribution of the molecules over the different quantum states in thermal equilibrium.

According to the Boltzmann equation, the number of molecules dN_E that have a classical vibrational energy between E and $E + dE$ is proportional to $e^{-\frac{E}{k_B T}} dE$, where k_B is Boltzmann's constant and T is the absolute temperature. In quantum theory, only discrete values, $E_{(\nu)}$, are possible for the vibrational energy. The number of molecules in each of the vibrational states is then proportional to the Boltzmann factor $e^{-\frac{E_{(\nu)}}{k_b T}}$. The zero-point energy can be left out, since to add this to the exponent would only result in a multiplication factor that would be the same for all the vibrational levels (including the zero level).

The thermal distribution of the rotational levels (unlike that of the vibrational levels) is not simply given by the Boltzmann factor. We must account for the fact that, according to quantum theory, each state of an atomic system with total angular momentum J consists of 2J+1 energy levels which are degenerate in the absence of an external field; that is, the state has a (2J+1)-fold degeneracy. The number of molecules N_J in the rotational level J of the lowest vibrational state at the temperature T is thus proportional to

$$N_J \propto (2J+1)\, e^{-\frac{F_{(J)} hc}{k_B T}} \tag{14.1.6.2.3.1}$$

where $F_{(J)}$ is the rotational term value (equal to $\frac{E_{(J)}}{hc}$). For sufficiently large T or small rotational constant B, the population of the J^{th} rotational level, for N molecules, is given by the following equation [see p. 125 in reference (3)]

$$N_J = N \frac{hcB}{kT} (2J+1)\, e^{-\frac{BJ(J+1)hc}{kT}} \tag{14.1.6.2.3.2}$$

Since the factor 2J+1 increases linearly with J, the number of molecules in the different rotational levels goes through a maximum before decreasing with the rotational quantum number. It can be shown[3] that this maximum lies at

$$J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2} \tag{14.1.6.2.3.3}$$

This expression clearly shows that J_{max} increases with decreasing B and increasing T. It should be noted that the number of molecules in the lowest rotational level, J = 0, is not zero. With increasing temperature, the band extends over a wider frequency range and the intensity maxima of the two rotational branches move outward and at the same time become flatter.

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase, as seen in Figure 5.4.2.2 .

From this relationship, we can also deduce that in heavier molecules, B will decrease because the moment of inertia will increase, and the decrease in the exponential factor is less pronounced. This results in the population distribution shifting to higher values of J. Similarly, as temperature increases, the population distribution will shift towards higher values of J.

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14.1.6.2.4: The Pure Rotational Spectrum has Unequal Spacings

Vibrational energy which is a consequence of the oscillations/ vibrations of the nuclei along inter nuclear axis, is possible only when the distance between the nuclei is not fixed/ rigid; that means the separation between the two nuclei is flexible/ elastic (non-rigid rotator). Consequently, centrifugal force, when the molecule is rotating, tends to fly the reduced mass μ away from the axis of rotation. To keep the mass rotating about the axis, there must be some restoring force to counter balance the centrifugal force. The work done to supply this force is stored as potential energy. Therefore, unlike the case of rigid rotator, total energy of rotation in a molecule comprises of kinetic and the potential energy corresponding to centrifugal force of rotation.

Let r_e is the distance between the nuclei when the separation is taken to be rigid and r_c under the action of the centrifugal force. According to Hook's law, restoring force is proportional to change in internuclear distance $(r_c - r_e)$, or $= k(r_c - r_e)$ which in turn, will be equal to the centrifugal force.

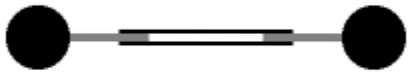


Figure 14.1.6.2.4.1: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is stationary. The connection between the weight consists of pistons. When the connecting pistons contract, the rotation rate goes up. When the inward force exerted by the pistons relaxes the weight slide outwards, and the rotation rate goes down. (Public domain; Cleonis).

Centrifugal force,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{14.1.6.2.4.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{14.1.6.2.4.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{14.1.6.2.4.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 14.1.6.2.4.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{14.1.6.2.4.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{14.1.6.2.4.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 14.1.6.2.4.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1+\Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{14.1.6.2.4.6}$$

$$= \frac{L^2(1-2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{14.1.6.2.4.7}$$

using

$$(1+\Delta r/r_e)^{-2} \approx (1-2\Delta r/r_e) \tag{14.1.6.2.4.8}$$

$$E_r = \frac{L^2}{2\mu\, {r_e}^2} - \frac{L^4}{k\mu^2\, {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu^2}{r_e}^6} \tag{14.1.6.2.4.9}$$

$$= \frac{L^2}{2\mu\, {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2\, {r_e}^6} \tag{14.1.6.2.4.10}$$

$$= \frac{\hbar^2\ J(J+1)}{2\mu\, {r_e}^2} - \frac{\hbar^4\ J^2(J+1)^2}{2k\mu^2\, {r_e}^6} \tag{14.1.6.2.4.11}$$

Use of Equation 14.1.6.2.4.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\,\sqrt{J(J+1)} \tag{14.1.6.2.4.12}$$

has been made to obtain relation in Equation 14.1.6.2.4.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{14.1.6.2.4.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\,\mu\, {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{14.1.6.2.4.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\,\mu^2\, {r_e}^6\, c}\ (\text{in cm}^{-1}) \tag{14.1.6.2.4.15}$$

First term in the Equation 14.1.6.2.4.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 14.1.6.2.4.3 wherein k is the spring constant that, as we will see in the following section, plays the same role as in the vibrational motion. In other words, centrifugal stretching constant $\tilde{D}$ is not only measures the influence of centrifugal force, but also hints upon the interaction between the rotational and vibrational motions.

Since $\tilde{D}$ is positive, it is clear from Equation 14.1.6.2.4.13 that the energy levels for the non-rigid rotator are slightly lower on energy scale than those of rigid rotator for the corresponding J values; the magnitude of decrease in energy of the non-rigid rotator states increases with J as shown in the Figure 14.1.6.2.4.2.

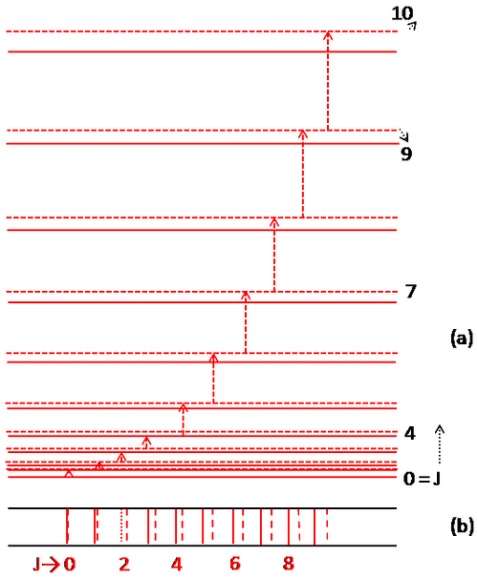


Figure 14.1.6.2.4.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

Consequently, on applying the selection rule $\Delta J = \pm 1$, rotational spectrum of a non-rigid rotator consists of a series of lines (red lines) wherein separation, unlike the case of spectral series (broken red lines) of a rigid rotator, between the consecutive rotational lines decreases with increase in J , as shown in the Figure 14.1.6.2.4.2. It may be noted that value of D is very small compared to B with the result that the influence of D is significant only for very large J values.

For example, for HCl the values are $B \sim 10.4 \quad cm^{-1}$ and $D \sim 0.0004 \ cm^{-1}$. Usually, D is ignored in the calculations. Figure 14.1.6.2.4.2 exaggerates the decrease in energy to visualize its effect. Nevertheless, non-rigid rotator is the model that describes the rotational motion more accurately and hence explains the spectral experimental observations not only in the microwave region but also the rotation-vibration spectra and the rotational structure of the electronic bands discussed in the later sections.

Contributors and Attributions

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14.1.6.2.5: Anharmonicity and Vibrational Overtones

Although the harmonic oscillator proves useful for modeling lower energy levels, like $v = 0, 1$, it fails at higher numbers of v. It not only fails to properly model atomic bonds and dissociations, but also is unable to match spectra showing additional lines that are not accounted for in the harmonic oscillator model.

Anharmonicity

Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to a transition of $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure 14.1.6.2.5.1). For example, the parabolic potential of the Harmonic Oscillator approximation means that the vibrations can hold any amount of energy and bonds can stretch to any length, while in real molecules if the atoms are too far apart the bond will dissociate.

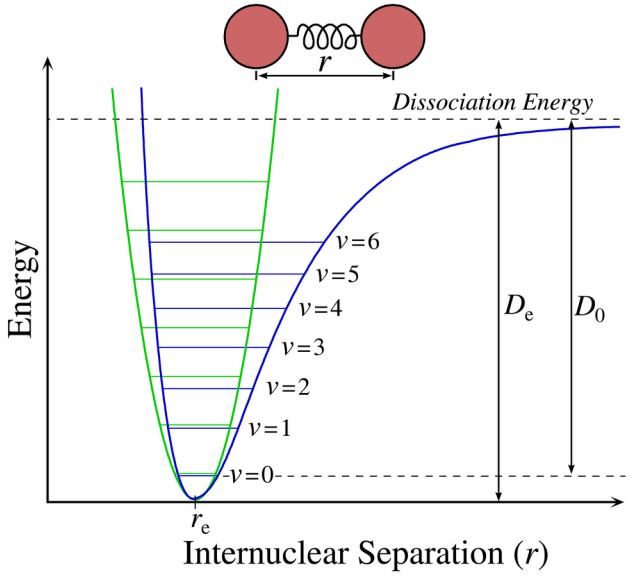


Figure 14.1.6.2.5.1 : Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension. (CC BY-SA 3.0; Created by Mark Somoza March 26 2006).

As you can see in Figure 14.1.6.2.5.1 , the harmonic oscillator potential well (in green) only roughly fits over the more accurate anharmonic oscillator well (in blue). The blue curve accounts for dissociation at large R values, which the green curve does not even remotely cover. However, this is just one important difference between the harmonic and anharmonic (real) oscillators.

The real potential energy can be expanded in the Taylor series.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \quad (14.1.6.2.5.1)$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

or in terms of a spring constant, ignoring the absolute energy term($V(R_e)$) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2$$

Alternatively, the expansion in Equation 14.1.6.2.5.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \tag{14.1.6.2.5.2}$$

where

- $V(x_0) = 0$, and $r = R - R_0$.
- k is the harmonic force constant, and
- γ is the first (i.e., cubic) *anharmonic* term

It is important to note that this approximation is only good for R near R_0.

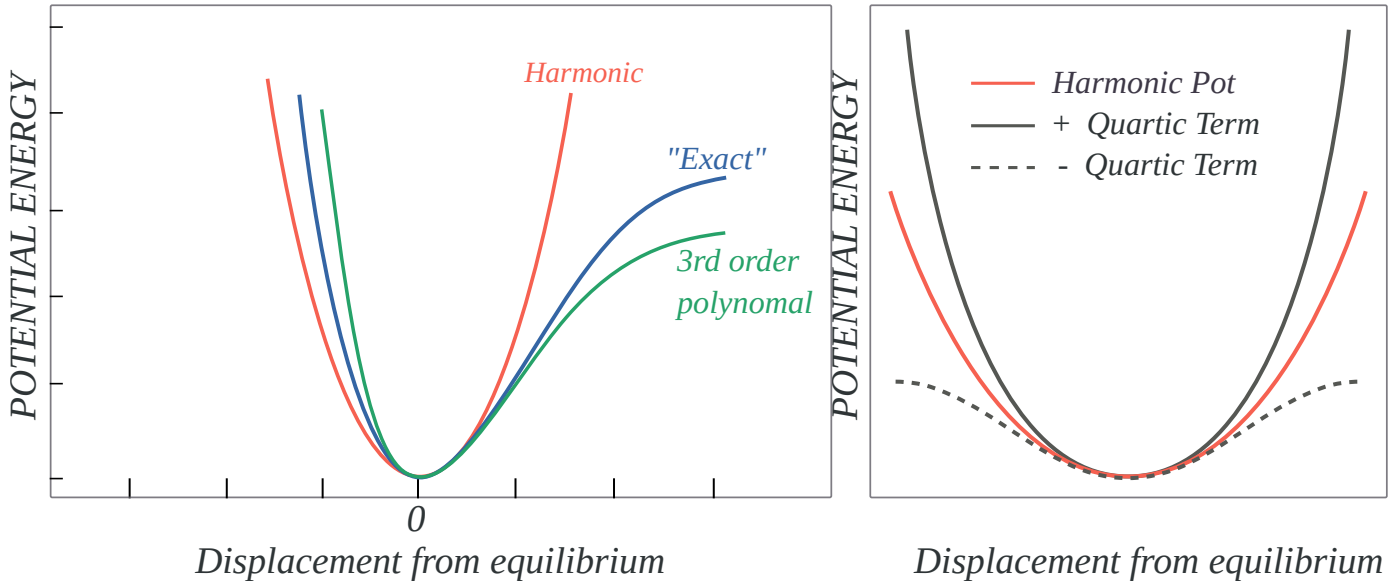


Figure 14.1.6.2.5.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

The harmonic oscillator approximation gives by the following energies:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right)$$

When the cubic term in the expansion (Equation 14.1.6.2.5.2) is included, and the Schrödinger equation is solved using perturbation theory this gives:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v + \frac{1}{2}\right)^2$$

where $\tilde{\chi_e}$ is the **anharmonicity constant**. It is much smaller than 1, which makes sense because the terms in the Taylor series approach zero. This is why, although E_v technically includes all of the Taylor series, we only concern ourselves with the first and second terms. The rest are so small and barely add to the total and thus can be ignored. To get a more accurate approximation, more terms can be included, but otherwise, can be ignored. Almost all diatomics have experimentally determined $\frac{d^2V}{dx^2}$ for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 have had terms up to $n < 10$ determined of Equation 14.1.6.2.5.1.

Overtones

The Harmonic Oscillator approximation predicts that there will be only one line in the spectrum of a diatomic molecule, while experimental data shows there is in fact one dominant line--**the fundamental**--and other weaker lines. How can we account for

these extra lines?

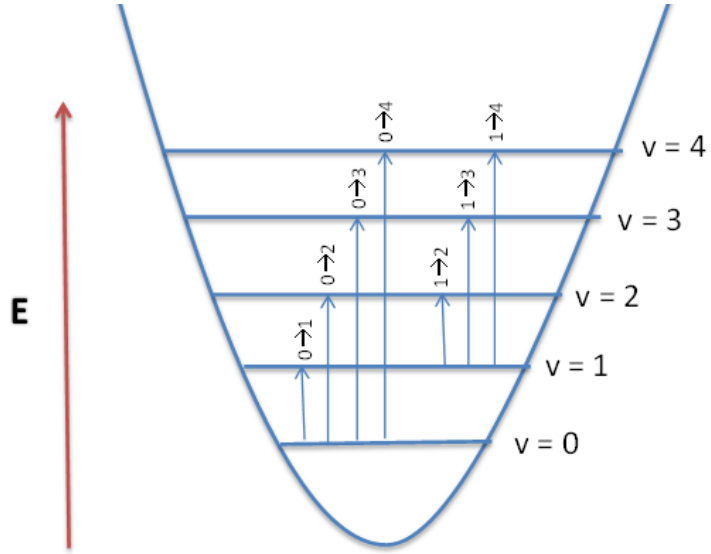


Figure 14.1.6.2.5.3 : A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (n > 1) are called hot transitions (hot bands).

Any resonant frequency above the fundamental frequency is referred to as an *overtone*. In the IR spectrum, overtone bands are multiples of the fundamental absorption frequency. As you can recall, the energy levels in the Harmonic Oscillator approximation are evenly spaced apart. Energy is proportional to the frequency absorbed, which in turn is proportional to the wavenumber, the first overtone that appears in the spectrum will be twice the wavenumber of the fundamental. That is, first overtone $v = 0 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

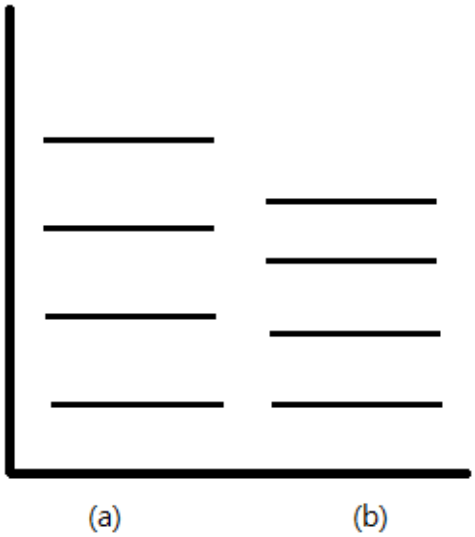


Figure 14.1.6.2.5.4 : An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, as implied by Figure 14.1.6.2.5.4. Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V = \text{any number}$. That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (the first overtone) or $v = 0$ to $v = 3$ (the second overtone). The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapidly decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be approximately v times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

This is demonstrated with the vibrations of the diatomic HCl in the gas phase:

Table $14.1.6.2.5.1$ *: HCl vibrational spectrum.*

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (third overtone)	10 923.1	11 543.6	10,907.4
$0 \rightarrow 5$ (fourth overtone)	13 396.5	14 429.5	13,370

We can see from Table $14.1.6.2.5.1$ that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of the transition occuring).

Exercise 13.5.1

HCl has a fundamental band at 2885.9 cm^{-1} and an overtone at 5668.1 cm^{-1} Calculate $\tilde{\nu}$ and $\tilde{\chi_e}$.

Exercise 13.5.2

Write out the Taylor series, and comment on the trend in the increasing terms. Using a test number x, please add terms 3, 4, and 5, then compare this to term 2. How do they compare? We have seen that the anharmonic terms increase the accuracy of our oscillator approximation. Why don't we care so much about terms past the second?

References

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14.1.6.3: Experimental and Instructions

Materials

- **Equipment:**
  - Nicolette iS50 FT-IR Spectrometer
  - Long Path Length Gas Cell with windows that are transparent to IR radiation (KBr windows)
- **Reagents:**
  - Hydrogen Chloride 99+%: Aldrich Chemical Company; Cat # 29,542-6; Cas # [7647-01-0]; FW = 36.46; safety information can be obtained from: Sigma Aldrich (Click).

HAZARD: This experiment uses concentrated HCl (strong acid)!

The concentrated acid used in this experiment is a hazard. Go to the linked Safety Data Sheet and read the safety information related to these compounds:

- Hydrogen chloride is **colorless, pungent, and corrosive** .
- Contact will cause **burns to the skin, severe burns to the eyes, and burns to the respiratory system if inhaled.**
- **Use gloves, protective eyewear, and avoid inhalation** throughout this experiment.

USE CARE: Gas Cells are FRAGILE and the KBr Windows are FRAGILE andare destroyed by water!

The cell is constructed of a glass body with KBr windows at each end. Ensure that the salt windows are kept free of moisture at all times. Please do not touch these windows.When not in use the IR gas cell must be stored in the desiccator.

The Group Notebook (ELN) Template is available through Google Classroom. This template is provided as a guide so that you know what data and information should be kept in a notebook. You may keep your personal notebook in any way you'd like, but you should translate your notes into this template for the group submission.

Part I: What can an FTIR Spectrum tell us about a diatomic gas molecule?

A: Computational prediction of vibrational frequency and bond length

1. Use a computational chemistry program to determine the computationally-predicted **vibrational frequency** and **bond length** of hydrochloric acid gas.
   a. **Perform Equilibrium Geometry Calculation:** Specifically, use density functional theory (DFT) to calculate the equilibrium geometry of HCl gas, determine its vibrational frequency (or frequencies), and the equilibrium bond length (internuclear distance).
   b. **Record Computational Results:** Record the predicted IR spectrum in your group notebook. Also record the predicted frequency of the vibration, the predicted bond length, and any other information you feel is worth recording.

Part IB: Preparation of sample and collection of FTIR spectrum

SEE HAZARD and CAUTION STATEMENTS above.

Use the following method (see video) of preparing a gas cell. Start with the cell filled only with the gases from atmosphere: collect **a spectrum of the background**. Then, add one drop of HCl, allow it to evaporate in the sealed cell, and use the cell to collect **a spectrum of HCl gas.**

Prepare the cell with background gas

1. Put on clean, dry gloves before handling any components of the gas cell.
   Avoid touching the Potassium Bromide (KBr) windows with bare hands, and never expose them to water, as they are made of salt and will degrade upon contact with moisture.
2. Gather all required materials, including:
   - One Pyrex gas cell body
   - Two Potassium Bromide (KBr) windows
   - Two blue end caps
   - Four O-rings
   - Two septa
   - pH paper
   - Concentrated hydrochloric acid
   - Glass pipettes
   - Wipes
3. Insert a small piece of pH paper into one of the inlets of the gas cell.
   Fold the pH paper as needed so that it fits easily inside the inlet.
4. Cap the inlet containing the pH paper with a septum.
   The septum does not need to fold down or form a tight seal; it simply needs to securely plug the opening.
5. Prepare the end caps by placing one O-ring into the groove inside each end cap.
   Use your thumb to press the O-ring evenly into the groove.
6. Place one Potassium Bromide window into each end cap.
   If a window has one side that appears etched or foggy, orient that side so it faces inward toward the cell body.
   Keep the windows dry at all times.
7. Place a second O-ring on top of each Potassium Bromide window.
8. Gently screw the body onto the end caps without distrubing the windows and o-rings.
   Do not overtighten. The Potassium Bromide windows are fragile and can crack or crush if excessive force is applied.
   Tighten only until slight resistance is felt.
9. Collect a background spectrum on the sealed gas cell assembly using the FTIR instrument.

Introduce HCl into the cell

10. Carefully introduce hydrochloric acid into the cell.
    Using a glass pipette, add **one drop** of concentrated hydrochloric acid through the inlet.
    Ensure that the liquid does not contact the Potassium Bromide windows.
    If any acid is spilled, clean it immediately and change your gloves before proceeding.
11. Wipe the outside of the inlet to remove any residual acid, then cap the inlet with a septum.
12. Gently move and rotate the cell so that the liquid drop moves away from the Potassium Bromide windows and toward the center of the cell.
    Rotate the cell slowly to spread the liquid around the inner circumference, increasing surface area and promoting evaporation.
13. Monitor the pH paper.
    The cell is ready when the pH paper indicates the presence of acid (e.g., a color change).
14. Collect the FTIR spectrum of gaseous hydrochloric acid.

Disassemble the cell and clean up

15. Disassemble the cell carefully after data collection.
    Remove at least one septum before unscrewing the end caps.
    Unscrew the end caps slowly, ensuring that the acid does not contact the Potassium Bromide windows.

16. Set the end caps aside carefully and keep the windows dry.
17. Remove the pH paper using a clean glass pipette and tap it out of the cell body.
18. Change your gloves before handling the Potassium Bromide windows! Transfer the windows to their designated storage location inside a desiccator.
19. Flush all remaining cell components thoroughly with water and dry them with a towel.
20. Wipe bench spaces that may have acid residue with a wet towel, followed by a dry towel.
21. Dispose of all acid-contaminated waste in the appropriate waste container.

Data Analysis for HCl FTIR spectrum for Part I

After collecting your first spectrum, please email your results to yourself, your group, and your instructors. Then assemble your group and begin group discussion and analysis of the data. The files linked at the top of this page will guide you to analyze the spectrum, derive mathematical models to fit the data, and calculate molecular parameters from the fits. (links copied here for convenience: Shared Files for Duke Students). Your instructors will be on hand to help guide you if you get stuck.

Part II: How does instrument resolution effect the certainty of derived parameters?

In Part II, you will collect the spectrum of HCl gas at different instrument resolutions to determine how instrument resolution affects what the IR spectrum can show us, and how instrument resolution affects the uncertainty in the results.

If you finish with part I early, you may be able to collect Part II data in the first lab period. Otherwise, data collection for Part II will happen in the second week of this module.

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14.1.6.4: References

1. Moore, W.J., Physical Chemistry, 4th ed., Prentice-Hall, Englewood Cliffs, New Jersey, 1972, pp. 767-770; or Pauling, L.; Wilson, E.B. Introduction to Quantum Mechanics, McGraw-Hill, New York, 1935.

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14.1.7: UNDER CONSTRUCTION

14.1.7.1: FTIR spectrum of HCl

14.1.7.2: Part I - Data Analysis

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14.1.7.9.11: Least Squares Linear Regression (1)

14.1.7.9.11.1: Rejection of Discordant Data

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14.1.7.9.12: Homework Problems

14.1.7.10: Rotation-Vibration Spectrum of HCl AND DCl; Vibrational Spectrum of SO2

14.1.7.10.1: Data Analysis

14.1.7.10.2: Prelaboratory Exercise

14.1.7.10.3: Transition Intensities

14.1.7.10.4: Part I - FTIR spectrum of a mixture of HCl and DCl gas

14.1.7.10.5: Part II - FTIR spectrum of SO2

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14.1.7.1: FTIR spectrum of HCl

Later in this semester, you will use a Fourier Transform Infrared (FT-IR) Spectrometer to investigate the coupling between the vibrational and rotational motions of a diatomic molecule, using hydrogen chloride (HCl) as the example. The FT-IR spectrum of HCl gas is a classic demonstration of quantum behavior. The diatomic, HCl, has only one IR-active vibrational mode. Yet, a close look at its IR spectrum shows interesting structure that can only be explained by quantization and coupling of the molecule's rotations to the vibrational motions.

This activity will help you get acquainted with MatLab, and it will also serve as a template for how you can approach data analysis later this semester. So, after you complete this, save your work and plan to use it again later!

> Be sure that the supporting files provided by our instructors are in your MatLab working directory. Using MatLab, open the "FTIR_StudentGuide.mlx" live script file, and follow the instructions in the document.

Below is an FT-IR spectrum of HCl gas (Figure 14.1.7.1.1). Since chlorine has two naturally-abundant isotopes, $^{35}\mathrm{Cl}$ and $^{37}\mathrm{Cl}$, the spectrum is actually the spectrum of $\mathrm{H}^{35}\mathrm{Cl}$ and $\mathrm{H}^{37}\mathrm{Cl}$. The taller set of peaks is from $\mathrm{H}^{35}\mathrm{Cl}$, while the shorter set of peaks is from $\mathrm{H}^{37}\mathrm{Cl}$.

FT-IR Spectrum of a mixture of HCl^{35} and HCl^{37}

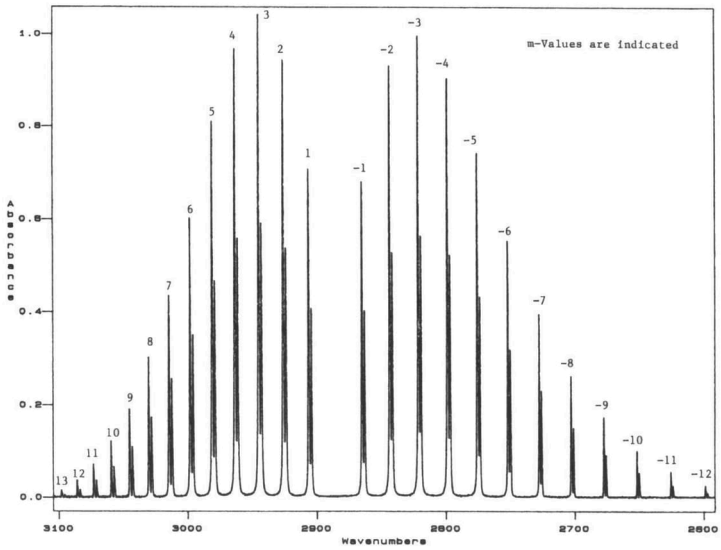


Figure 14.1.7.1.1: FTIR Spectrum of HCl. (CC-NC-BY; DUKE CHEM)

Table of Peak Energies in wavenumbers:

Table $1: \tilde{\nu}_{(m)}(cm^{-1})$ *for HCl from m = 4 to -4*

$\tilde{\nu}_{(m)}(cm^{-1})$	m	isotope HCl^{35} or HCl^{37}
2963.01		
2960.84		
2944.57		
2942.52		
2925.65		
2923.48		
2906.00		
2903.95		
2864.78		
2862.85		
2843.33		
2841.40		
2821.27		
2819.34		
2798.61		
2796.80		

1. Determine from Figure $14.1.7.1.1$ which peaks arise from $H^{35}Cl$ and which peaks arise from $H^{37}Cl$ and give each pair of peaks an appropriate m value.
2. Enter the peak positions $\tilde{\nu}_{(m)}$ for $H^{35}Cl$ and $H^{37}Cl$ as two separate vectors into Matlab.
3. Create a corresponding vector of m values from +4 to –4.
4. For each isotope, use Matlab to calculate the separation between adjacent peaks $\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)}$.

   Note

   $\Delta\tilde{\nu}_{(m)}$ cannot be calculated for m = –1 since there is no peak for m = 0

5. For each isotope, $H^{35}Cl$ and $H^{37}Cl$, do a separate plot of $\Delta\tilde{\nu}_{(m)}(cm^{-1})$ (y-axis) versus m (x-axis) with each data point indicated by a small circle.

   Note

   When plotting an x-y graph, the vectors x and y must be the same length. If $\Delta\tilde{\nu}_{(m)}$ cannot be calculated for a particular m value (see step (4)), then that value of m must be deleted from the vector of m values.

6. Perform a linear least-squares regression analysis and determine the slope, y-intercept, and standard deviation in the slope and intercept.
7. Create a final plot for each isotope, $H^{35}Cl$ and $H^{37}Cl$, that includes the raw data and the least-squares fitting.

Save your work!

When you have completed the steps above and have created a final plot, it is a good idea to get feedback from your instructors to confirm that you have successfully created a "full-credit" plot. Then, please export your work, inlcuding the final plot, as a pdf file and move to the next section.

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14.1.7.2: Part I - Data Analysis

Data Analysis for HCl/DCl FTIR spectra

Note

This is one of the more laborious data analyses you will do this semester. Let's minimize the number of repetitive tasks to save you some time. The following shortcuts are recommended:

- **Collaborate with a partner on steps 1-3 (allowed in this specific case only)**:You may collaborate with your lab partners in steps 1-3 below. One student should work up the data (steps 1-3 ONLY) for $H^{35}Cl$ and $H^{37}Cl$, and the second student should do the same analysis for $D^{35}Cl$ and $D^{37}Cl$. You should then share your graphs of $\Delta\tilde{\nu}_{(m)}$ versus m and the values determined for the slopes and y-intercepts of these plots. Each student should do one complete analysis (either HCl or DCl) alone, and the other analysis can be the work of a partner. However, you are responsible for all work that is in your ELN, so be sure your partner's work is correct. *Steps 4 and onward should be completed individually, as usual.
- **Calculate errors for one isotope only**: The propagation of errors that you calculate for one isotope should similar (perhaps not identical, but close enough) as for another isotope. Save time by propagating errors carefully for (B_e, α_e, $\tilde{\nu}_o$, Ie, re, and k for one isotope, then use those errors as an approximation for the errors for analogous values for other isotopes.
- **Use what you know!** Do you remember that MatLab Introduction module way back in the beginning of this course? It was a long time ago, but it was a template for data analysis in this module! Go back and use what you already know, and what you already created as a template, for this data analysis.

Collaborate with a partner

1. Label each peak in your spectra as "P" or "R" and its J-value as: P(1), P(2),..., R(O), R(1),... etc., as shown in Figure 2 on page 399 of Shoemaker, Garland and Nibler. (**Note:** Spectra recorded using your iS50 FTIR spectrometer are plotted with the wavenumber (abscissa) decreasing from left to right.)
2. For each of the four isotopic combinations ($H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$), make a table of the m values and the corresponding peak frequencies $\tilde{\nu}_{(m)}$. For each isotopic combination, calculate the separation between adjacent peaks.

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} \tag{14.1.7.2.1}$$

Note

$\Delta\tilde{\nu}_{(m)}$ cannot be calculated for m = –1 since there is no peak for m = 0. Therefore m = –1 must be deleted from the vector of m values.

3. Plot the differences between adjacent absorption frequencies (i.e., $\Delta\tilde{\nu}_{(m)}$ versus m. Then perform a linear least squares fit of the data with the understanding that

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} = (2B_e - 3\alpha_e) - 2\alpha_e m \tag{14.1.7.2.2}$$

Use the standard deviations of the slope and intercept in your error analysis (Q14).

Work on your own

4. **Compute** B_e **and** α_e for each isotope from the intercept $(2B_e - 3\alpha_e)$ and the slope $-2\alpha_e$ of each best fit line (Equation 14.1.7.2.2).
5. **Calculate the frequency of the forbidden transition** $\tilde{\nu}_o$ using your calculated values of B_e and α_e. To do this, use equation 9 in expt 37 of Shoemaker, Garland and Nibler. The equation is $\tilde{\nu}_m = \tilde{\nu}_o + (2B_e - 2\alpha_e)m - \alpha_e m^2$. Calculate $\tilde{\nu}_o$ from several of the lines with low m values. Calculate the average value, and standard deviation, of $\tilde{\nu}_o$.

> **Note**
>
> You will get the best results by using only the lines closest to the center (e.g., m = ±1, ±2).

6. **Create a table** of $\tilde{\nu}_o$, B_e, and α_e for the four isotopic combinations The units should be cm^{-1}.
7. **Calculate the moment of inertia (I_e), and the internuclear distance (a.k.a. equilibrium bond length, r_e)** for all four isotopic combinations.
8. **Calculate the harmonic oscillator force constant,** k, for each isotopic combination from your calculated values of $\tilde{\nu}_o$. In doing so you will need to assume that $\tilde{\nu}_o$ and the harmonic oscillator frequency $\tilde{\nu}_e$ are the same, thus ignoring the effects of anharmonicity (see the formulas and discussion on pages 400 and 401 of Shoemaker, Garland and Nibbler).
9. **Compare your values of r_e and k with those reported in the literature.** Why are these values independent of isotopic substitution?
10. **Determine the isotope effects:** Compute the ratios $\frac{\tilde{\nu}_o^*}{\tilde{\nu}_o}$ and $\frac{B_e^*}{B_e}$ for ^{35}Cl and ^{37}Cl in the case of HCl, and again in the case of DCl. Compare these with the predicted values given by Eqs. (11) and (13) on page 400 of Shoemaker, Garland and Nibbler.
11. From the results in 10, above, **explain why is the ^{35}Cl /^{37}Cl isotope effect so much larger in DCl than it is in HCl?** That is, when looking at your FTIR spectrum, the ^{35}Cl/^{37}Cl line separation is significantly greater in the DCl case then when compared to the HCl case. A descriptive answer is a good start, but your experimental observations should also be supported with a calculation that justifies the experimental observation.
12. Apply the Boltzmann distribution to explain observed band intensities in terms of the populations of the ground-state levels (see section 4.2). Again, a descriptive answer is a good start, but it should be supported with calculated results. You might create a spreadsheet to do these calculations. Does a calculation based on the Boltzmann population of rotational states match what you see experimentally in terms of which rotational lines show the greatest intensity?
13. From the mean line intensities for at least 10 features (for example five or more lines from the HCl spectrum and five or more from the DCl spectrum for a total of at least 10), determine the relative abundance of the two Cl isotopes. Estimate the weighted average atomic mass of Cl (that you might see on a periodic table for example) assuming that ^{35}Cl and ^{37}Cl have masses of 34.968 and 36.956 amu, respectively. Compare your result with the reported atomic mass of Cl.
14. For <u>one</u> isotope only, calculate the estimated uncertainty in each of the parameters determined for this experiment (B_e, α_e, $\tilde{\nu}_o$, I_e, r_e, and k). (Another table would be helpful)
15. Why is it important to purge the sample compartment of the FTIR spectrometer for both the background and sample runs? Why is it important to purge both background and sample for the same amount of time?

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14.1.7.3: Part I - References

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14.1.7.4: Part II - Data Analysis

4.7.1. Assign the fundamental bands of SO_2 as: symmetric stretch, $\tilde{\nu}_1$; bend, $\tilde{\nu}_2$; asymmetric stretch, $\tilde{\nu}_3$; and, report their frequencies. Compare your value with those reported in the literature.

4.7.2. Then assign any other bands, comparing the observed frequencies with those calculated from combinations of the fundamental values $\tilde{\nu}_1$, $\tilde{\nu}_2$, $\tilde{\nu}_3$.

4.7.3. Calculate k_1 and $\frac{k_\delta}{\ell^2}$ from Equations (1) and (3) (on page 385 of Shoemaker, Garland and Nibler) using your values of $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_3$. Check the valence-force model by calculating both sides of Eq. (2) (also on p. 385 of Shoemaker) and comparing them. Again, compare your results with literature values.

Note

When finding literature values for the force constants of SO_2, you will likely notice that different notations are used. It may be difficult to find the k_1 and $\frac{k_\delta}{\ell^2}$ notation used in Shoemaker, Garland and Nibler (and as such in this manual). For example, Kivelson[8] reports these same vales as f_d; and, $\frac{f_a}{d^2}$ and reports the values in units of $\frac{dynes}{cm}$ rather than $\frac{N}{m}$. Be prepared to convert.

4.7.4 Using your values of $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_1$, calculate $\tilde{C}_{v(vib)}$ at 298 K and at 500 K from Eq. (8) on page 386 of Shoemaker, Garland and Nibler.

4.7.5 At these same temperatures, calculate $\tilde{C}_v$ from the expression

$$\tilde{C}_v = 3R + \tilde{C}_{v(vib)} \tag{14.1.7.4.1}$$

and compare your results with the following $\tilde{C}_v$ values (obtained from directly measured values of $\tilde{C}_p$ and the expression

$$\tilde{C}_v = \tilde{C}_p - R \tag{14.1.7.4.2}$$

$\tilde{C}_v$ = 30.5 J K^{-1} mol^{-1} at 298 K and 37.7 J K^{-1} mol^{-1} at 500 K.

4.7.6 Calculate the uncertainty of each result you report in this experiment.

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14.1.7.5: Part II - References

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6. Colthup, N.B., Daly, L.H., and Wiberley, S.E. Introduction to Infrared and Raman Spectroscopy, 3rd ed., Academic Press, Boston, 1990.

7. Shoemaker, D.P.; Garland, C.W.; Nibler, J.W. Experiments in Physical Chemistry, 6th ed., McGraw-Hill, New York, 1996, Chapter XIV, Experiments 35 and 37.

8. Kivelson, D., *The Determination of the Potential Constants of SO_2 from Centrifugal Distortion Effects,* J. Chem. Phys., 22 (5), 904, **1954.**

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14.1.7.6: Emission Spectrum of Iodine Vapor

This semester, you use a laser spectrometer to investigate the Molecular Spectroscopy of Iodine Vapor. In this assignment you will plot the electronic potential energy curves (Morse potentials) for the iodine molecule. A discussion of the terms used in this assignment can be found in your textbook (D. A. McQuarrie, and J. D. Simon "Physical Chemistry: A Molecular Approach", University Science Books, CA, 1997, Chapter 13, Section 13.1-13.7.

The functional form of the ground and excited state Morse potential wells for iodine molecule I_2 are given by the expression

$$V(R) = T_e + D_e\left[1 - e^{-a(R-R_e)}\right]^2$$

where V(R) is the potential energy of the system (y-axis), R is the interatomic separation (x-axis) between the iodine atoms, and T_e, and D_e, a and R_e are constants. Literature values for these constants are given below.

Constant	Ground State	Excited State
T_e	0 (cm^1) (arbitrarily set)	15730 (cm^1)
D_e	12244 (cm^1)	4112 (cm^1)
a	1.87 $\left(\mathring{A}\right)^{-1}$	2.00 $\left(\mathring{A}\right)^{-1}$
R_e	2.67 $(\mathring{A})$	2.97 $(\mathring{A})$

1. Generate a vector R that varies between 2 and 6 Å, in increments of 0.01 Å.
2. For both ground and excited states, calculate V(R) for each value of R using the above expression and the constants from the table. **NOTE:** These constants should be used in the units given above. No conversions are necessary.
3. On the same graph, plot V(R) (y-axis) versus R (x-axis), for both ground and excited states. Rescale the axes using the following axis scales:
   - V(R): 0 – 22500 cm^{-1}
   - R: 2 – 6 Å
4. Assemble a pdf document that contains both this assignment and the FTIR assignment into one pdf document and submit your work on Gradescope.

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14.1.7.7: Practice using a custom script

Install a custom script

The custom scripts (files with .m extension) and binary files (files with .mat extension) for this course are available here (click to go to OneDrive) using your Duke NetID. If you are using the Chemistry Department *bohr* server to access Matlab, the scripts are already installed for you.

If you are using your own computer, the scripts and binary files should be added to the correct folder on your computer. Follow the instructions in this video to install the lsq script, which performs least squares analysis.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Practice using a custom script and a binary file

This is an exercise to give you some practice in using Matlab to analyze data provided in a binary file, and plot the results using a custom script for least squares analysis. Before you start, make sure the custom files lsq.m and expt-1.mat are in your working MatLab directory (see video above). The binary file "expt-1" simply contains pre-defined 80 x 1 vector matrixes "x" and "y". This is just to save you the hassle of typing in the values for each vector.

> One way to work through this activity is to open the "Practice_LiveScript_XXX.mlx" file, and simply follow the instructions within the Live Script document.

Follow the steps below (there is a video below to walk you through these steps):

1. Open the MatLab program and be sure that you are working in the directory containing the lsq script and expt-1 binary file.
2. Type the following: **load expt-1**
   Your workspace now contains two variables, x and y which obey the following relation:
   $$y = Ae^{-Cx} \tag{14.1.7.7.1}$$
3. Plot y (ordinate) versus x (abscissa). Using Matlab, recalculate your data in linear form (ln y versus x) and plot the result. Using least squares analysis of the linearized data, calculate the values of A and C and report the standard deviation in these values. Using your calculated values of A and C, use Matlab to draw (a) the least-squares fitted line through your linear plot and (b) the best fit curve through your exponential plot. (NOTE: data should appear as points using the symbol 'o' and least squares fitted lines should be solid lines.)

   > **Expectation for a full-credit plot:**
   >
   > - Data is plotted in scatter format.
   > - Axes are correctly labeled, with correct units.
   > - When appropriate, a curve fit to the data is shown
   >   - equation of the line is shown on the plot, but not obscuring the data

        - uncertainty in slope and intercept provided
        - correlation coefficient (R) provided
    - Approrpate units are given for every value and every axis label.
    - Plot is centered on graph.
    - Text is easily readable (usually this means it is large enough to read easily.

4. You should show the plots described in (3) together with the values of A and C to your instructor. Each graph should have a title, and the x- and y-axes should be labeled.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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14.1.7.8: MATLAB PRACTICE (IN CLASS ACTIVITY)

Note

Before attempting these exercises, please make sure you have access to a working copy of the MatLab software and you have the custom scripts and binary files installed in the MatLab directory. If you are using FastX to access MatLab on campus, these files are already installed for you on the server. Otherwise, you should install MatLab and the custom files on your computer before proceeding.

The practice exercises in this module are meant to be completed during the scheduled meeting. The Matlab practice exercises are are designed to help you become literate in MatLab programing language and the MatLab GUI's so that you can accomplish the data analysis in this course. MatLab is the preferred tool for data analysis for the modules later in this lab semester.

Both of the activities below can be completed during the first laboratory meeting; collaboration among students is welcome, though each of you should complete the activity and submit your own work. Your work should be inspected by your teaching assistant (TA) before you submit the assignments and leave for the day. If your TA determines that you have done the activities correctly, you will receive full credit for this assignment.

14.1.7.8.1: The Basics

14.1.7.8.2: Practice with LiveScript

14.1.7.8.3: MatLab for Data Analysis In This Course

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14.1.7.8.1: The Basics

Originally Created by Lindsay Pederson, Fall 2022 | Modified by Kathryn Haas each semester since.

Caution

This exercise may be an uncomfortable experience if you haven't completed the basic MATLAB tutorials that were part of your pre-lab assignment. If you are feeling lost during this activity, please go back to the basic MATLAB tutorials to get comfortable with the basic commands and practice working with matrices before returing to this exercise.

MatLab General Layout

Open the MatLab program to begin. If the layout of your MatLab window looks different than the arrangement illustrated below, you can switch to the default layout using the "Layout" button in the Home Tab toolbar (see below). Choose "Default Layout" from the "Layout" drop down menu. If the layout still seems different than what is shown it might be because you have a Script or LiveScript file open in your MatLab program.

Compare your MatLab window to what is shown below. Read the figure below and familiarize yourself with the panels of the MatLab window. Then follow the instructions.

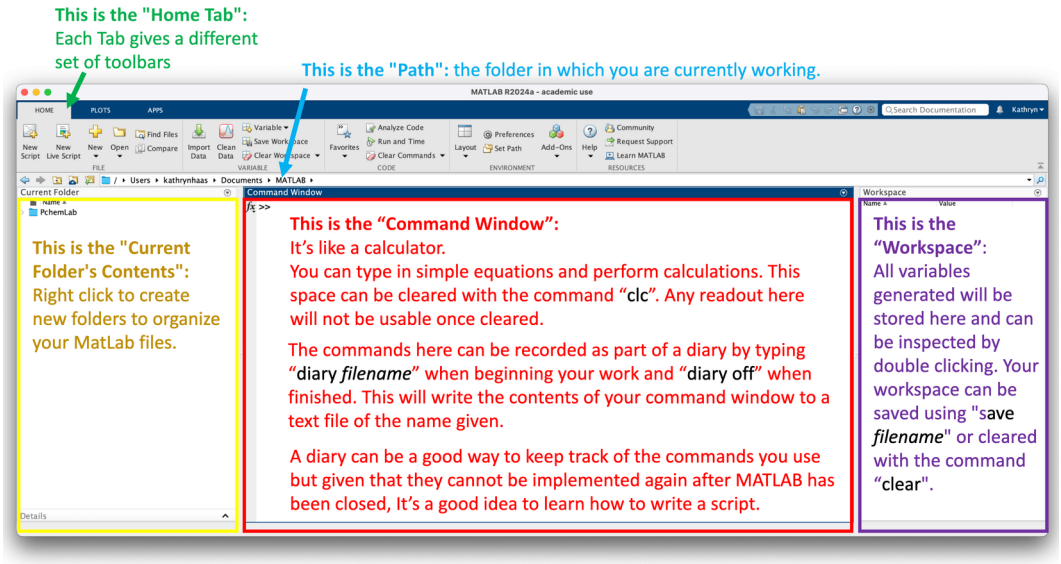


Figure 14.1.7.8.1.1: The default layout of the MatLab window (as of version R2024a). The tabs above the top toolar give access to different toolbar options. The file path is shown under the top toolar and indicates the current working folder. The Current folder's contents is shown in the pannel on the left. The center window is the Command Window, which functions like a calcuator. Type commands into the command window, save the work in the command window using the "diary filename" command to start saving and "diary off" when finished. All variables enterend in the Command Window will be populated in the Workspace, shown in the panel on the right. The Workspace can be saved using the "save filename" command or by using the "save workspace" button in the Home Tab toolbar. The workspace can be cleared using the "clear" command. (CC-NC-BY-SA; Kathryn Haas)

Practice with the Command Window

Find the command window in MATLAB. The command window is like a calculator. You can type simple equations here to perform calculations. The command window can be cleared by the command:

```
clc
```

All work is lost after the space is cleared.

The commands entered in the command window can be recorded in a text file (a diary). To record a diary, use the command "diary filename" at the beginning of your work:

```
diary filename
```

And then then at the end of the work:

```
diary off
```

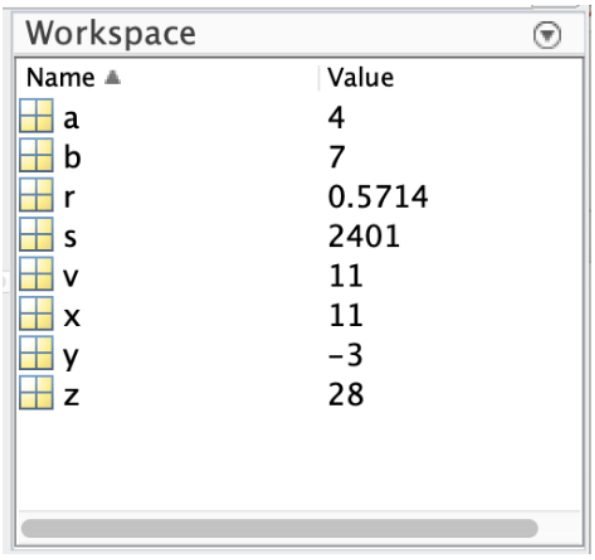
The diary file is a good way to keep track of commands, but the work cannot be implemented again from the diary file, so it has limited utility. **Script** and **Live Script** files are a much more useful way to record your work. **First, let's practice using the command window:**

Using the command window, begin a diary file with the name "practice_diary". Then do the following:

1. Clear the workspace by typing the clear command.
2. Create a variable *b* and set it equal to 7
3. Create a variable *a* and set it equal to 4
4. Add *a* and *b* and assign the result as *x*
5. Subtract *a* and *b* and assign the result as y
6. Multiply *a* and *b* and assign the result as *z*
7. Divide *a* by *b* and assign the result as r
8. Find *b* to the power of *a* and assign the result as s
9. Use the up arrow key to go back to the the command from step 4. Edit the command to assign it as *v* istead of *x* and end the command a semicolon; What does the semicolon do?
10. End the diary
11. Clear the command window with clc

The workspace

Notice that your workspace now contains all variables you defined. The workspace should look like this:



You can save the variables in the workspace as a binary ".mat file" with the command:

```
save filename
```

Use the command window to save your workspace using the file name "practice_workspace.mat". Notice the new file shows up in

the **Current Folder Window**.

Now, clear the workspace with the clear command.

```
clear
```

Just for practice, use the load command to load the file you just saved and inspect the workspace:

```
load filename
```

Clear the workspace again before moving to the next section.

Discussion Questions14.1.7.8.1.1

1. Where was the practice_diary file saved and what extension does it have? How would you submit a file like this to Gradescope?
2. When mathematical operations are performed in the command window, how are they defined in the workspace? What happens to the previous value in the workspace when you enter a new operation? (eq, try a + b , then a^b)
3. What does a semicolon at the end of a command do?
4. What does a percentage sign at the beginning of a line do?

Practice with Script Files

The Command Window is convenient for quick operations that you don't want to save. But it has some big limitations. For example, even if you do save the diary, you can't re-run any of the commands automatically. A better way to save your work is by entering it in a Script File.

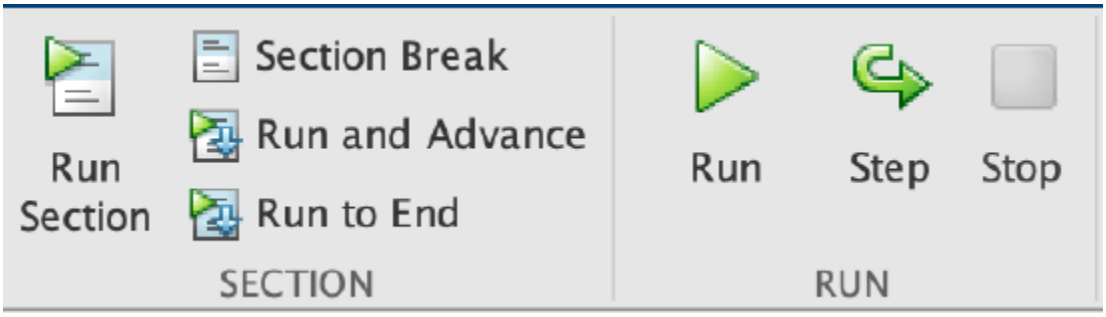
One way to start a new script is to go to the Home Tab and select **New**, then **Script**. Instead, let's use the command line to start a new script called "reference_script.m". Type the following into the command window:

```
edit reference_script.m
```

This will create a new script file. The new file should appear in the Current Folder window and it will open as a new tab in the Editor Window.

Find the Editor Window. In the Editor window, type the following:

```
%% Editor Exercises %%
% single percent sign indicates a text line
% double %% percent (only) indicates a section break.
% you can run each section of the editor by pressing the Run Section button.
% you can run the entire editor by pressing the Run button
```



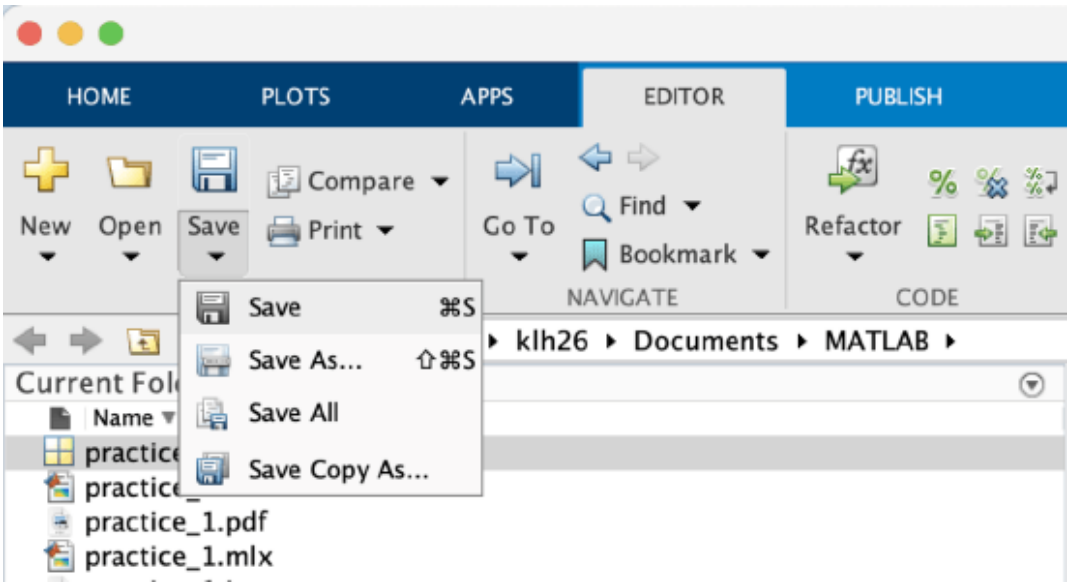

```
%%
%Type this into the new script in the Editor
b = 7
a = 4
```

```
% then hit run.
```

Notice what happens in the command window and in the workspace.

```
% again, type these examples of simple operations into the editor
x = a+b
y = a-b
z = a*b
r = a/b
s = b^a
% hit run and look at the command window
% then clear the command window and clear the workspace
% then add semicolons to the end of the lines and hit run again
```

Now that we see how the editor works, let's save the contents of the editor window as "reference_script.m". Go to the Editor tab and choose save.



At the end of the script that you just saved, add the following. Then run each section to see what happens. You can view any variables by typing their name in the command window.

```
%%
%% Building a reference sheet %%
a = 7;
b = 4;

%%
%Simple matrix - you can use spaces or commas to separate entries%
l = [1 2 3];
%%
%multiple rows - separated by semicolons%
m = [1;2;3];
%%
%matrices can have expressions in them%
n = [a+b, a-b, a*b];
%%
%transpose matrices with an apostrophe%
N = n';
%%
%multiply matrices
L = l*m;
M = m.*N;
```

```
%works the same with division
%%
%Create a matrix with regularly spaced intervals - defaults to one if not
%otherwise specified%
e = [1:16];
E = [1:0.5:16];
%%
%To reference specific elements of a matrix, call the matrix and then add
%coordinates (row, column) or just one number if it's a vector%
e7 = e(7);
m2 = m(2);
%%
%delete specific elements of a matrix
h = [1 2 3;4 5 6;7 8 9];
h(2) = [];
%check value of h in workspace
%%
%How to plot stuff
%you can just say "plot" but to intentionally keep track of figures it's a
%good idea to invoke figures by number
x = [1 2 3 4 5];
y = x.^2;
z = y./2;
figure(1)
hold on
plot(x,y)
plot(x,z,"o")
hold off
A = [1, 5, 0, 20];
axis(A)
xlabel('x')
ylabel('x^2')
title('Example')
%you can get help for any function you want to use (ex: plot()) by searching
%in the "Search Documentation" box at the top right of the screen
```

Save your files. Then clear the workspace and command windows before proceeding to the next section.

Discussion Questions14.1.7.8.1.2

1. What is the purpose of the period in the following statement? What happens if the period is removed?

   ```
   M = m.*N;
   ```

2. How can you delete the value 0.4 in the following matrix?

   ```
   mat1 = [0.1 0.2 0.3 0.4 0.5 0.9 1.0];
   ```

3. What does the "o" specification do in the code below:

   ```
   plot(x,z,"o")
   ```

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14.1.7.8.2: Practice with LiveScript

Install a custom script

The custom scripts (files with .m extension) and binary files (files with .mat extension) for this course are available here (click to go to GoogleDrive) using your Google account. If you are using the Chemistry Department *bohr* server to access Matlab, the scripts are already installed for you.

If you are using your own computer, the scripts and binary files should be added to the correct folder on your computer. Follow the instructions in this video to install the lsq script, which performs least squares analysis.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Practice using a custom script and a binary file

This is an exercise to give you some practice in using Matlab to analyze data provided in a binary file, and plot the results using a custom script for least squares analysis. Before you start, make sure the custom files lsq.m and expt-1.mat are in your working MatLab directory (see video above). The binary file "expt-1" simply contains pre-defined 80 x 1 vector matrixes "x" and "y". This is just to save you the hassle of typing in the values for each vector.

> Open the "Practice_LiveScript_XXX.mlx" file, and simply follow the instructions within the Live Script document.

The file linked above will walk you through the following steps to create a "final" plot.

1. Open the MatLab program and be sure that you are working in the directory containing the lsq script and expt-1 binary file.
2. Type the following: **load expt-1**
   Your workspace now contains two variables, x and y which obey the following relation:
   $$y = Ae^{-Cx} \tag{14.1.7.8.2.1}$$
3. Plot y (ordinate) versus x (abscissa). Using Matlab, recalculate your data in linear form (ln y versus x) and plot the result. Using least squares analysis of the linearized data, calculate the values of A and C and report the standard deviation in these values. Using your calculated values of A and C, use Matlab to draw (a) the least-squares fitted line through your linear plot and (b) the best fit curve through your exponential plot. (NOTE: data should appear as points using the symbol 'o' and least squares fitted lines should be solid lines.)

   > **Expectation for a "final" full-credit plot in this course:**
   >
   > - Data is plotted in scatter format.
   > - Axes are correctly labeled, with correct units.
   > - When appropriate, a curve fit to the data is shown
   >   - equation of the line is shown on the plot, but not obscuring the data
   >   - uncertainty in slope and intercept provided

    - correlation coefficient (R) provided
  - Approrpate units are given for every value and every axis label.
  - Plot is centered on graph.
  - Text is easily readable (usually this means it is large enough to read easily.

4. You should show the plots described in (3) together with the values of A and C to your instructor. Each graph should have a title, and the x- and y-axes should be labeled.

This is an old video of this activity (before LiveScript files were developed.)

YouTube Video

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14.1.7.8.3: MatLab for Data Analysis In This Course

MatLab is the preferred tool for data analysis in this course. That means that we will provide MatLab templates for your data analysis in each module and we can provide some basic support for your computational work if you use MatLab. However, if you have a favorite tool that is not MatLab, you are welcome to use it instead from now on, but please know that your instructional team may not be able to offer technical support for other computational programs.

We provide the MatLab Live Script files that can support your work in the modules this semester. Let's take a close look at the one for your "Error Analysis" problem set (your next assignment, in Module 3).

With any time remaining in the class meeting, or with your time out of class, access the MatLab files for this course and find the "Treatment of Error folder". From this folder, open the file called "Error_StudentGuide_date.mlx" and follow the instructions within to begin completing your next assignment. Also proceed to the next module (Module 3) in this manual to view the pre-lab assignment for your next meeting.

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14.1.7.9: THE TREATMENT OF EXPERIMENTAL ERROR

Learning Objectives

After completing the readings and practice problems recommended in this module, you should be able to:

- Describe and give examples of the following types of error that effect physical measurements, and identify the types of errors that affect precision and those that affect accuracy.
  - Gross / personal error
  - Systematic error
  - Random error
  - Determinate error
  - Indeterminate error
- Describe strategies for optimizing the accuracy of physical measurements and evaluating the precision of physical measurements.
- Identify the sources of random error in a measurement.
- Propagate error using mathematics.
- Report values and their precision in the proper form (applying the rules of significant figures to correctly indicate precision).

14.1.7.9.1: Characterizing Experimental Errors

14.1.7.9.2: Estimating and Reporting Error (Statistics, Propogation, and Rounding)

14.1.7.9.3: Least Squares Linear Regression

14.1.7.9.4: Rejection of Outliers (Q-test)

14.1.7.9.5: Guidelines for Recording and Reporting Data in your ELN

14.1.7.9.6: References and Additional Reading

14.1.7.9.7: Pre-lab Assignment

14.1.7.9.8: Learning Objectives, Important Info

14.1.7.9.9: Characterizing Experimental Errors (1)

14.1.7.9.10: Propagation of Uncertainty

14.1.7.9.11: Least Squares Linear Regression (1)

14.1.7.9.11.1: Rejection of Discordant Data

14.1.7.9.11.2: Weighted Least Squares Analysis

14.1.7.9.11.3: References

14.1.7.9.12: Homework Problems

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14.1.7.9.1: Characterizing Experimental Errors

In this course, you will need to determine the confidence in your results by doing appropriate error analysis. This section and the next are meant to review the types of experimental errors that affect accuracy and precision and to remind you of the simple methods for propagating error.

Errors That Affect Accuracy

Accuracy is how close a measure of central tendency is to its expected value, μ. We express accuracy either as an absolute error, *e*

$$e = \overline{X} - \mu \tag{14.1.7.9.1.1}$$

or as a percent relative error, %*e*

$$\%e = \frac{\overline{X} - \mu}{\mu} \times 100 \tag{14.1.7.9.1.2}$$

Although Equation 14.1.7.9.1.1 and Equation 14.1.7.9.1.2 use the mean as the measure of central tendency, we also can use the median.

> The convention for representing a statistical parameter is to use a Roman letter for a value calculated from experimental data, and a Greek letter for its corresponding expected value. For example, the experimentally determined mean is $\overline{X}$ and its underlying expected value is μ. Likewise, the experimental standard deviation is s and the underlying expected value is σ.

We identify as determinate an error that affects the accuracy of an analysis. Each source of a ***determinate error*** has a specific magnitude and sign. Some sources of determinate error are positive and others are negative, and some are larger in magnitude and others are smaller in magnitude. The cumulative effect of these determinate errors is a net positive or negative error in accuracy.

> It is possible, although unlikely, that the positive and negative determinate errors will offset each other, producing a result with no net error in accuracy.

We assign determinate errors into four categories—sampling errors, method errors, measurement errors, and personal errors—each of which we consider in this section.

Sampling Errors

A determinate sampling error occurs when our sampling strategy does not provide a us with a representative sample. For example, if we monitor the environmental quality of a lake by sampling from a single site near a point source of pollution, such as an outlet for industrial effluent, then our results will be misleading. To determine the mass of a U. S. penny, our strategy for selecting pennies must ensure that we do not include pennies from other countries.

> An awareness of potential sampling errors especially is important when we work with heterogeneous materials. Strategies for obtaining representative samples are covered in Chapter 5 of Harvey's Analytical Chemistry text on LibreTexts.

Method Errors

In any analysis the relationship between the signal, S_{total}, and the absolute amount of analyte, n_A, or the analyte's concentration, C_A, is

$$S_{total} = k_A n_A + S_{mb} \tag{14.1.7.9.1.3}$$

$$S_{total} = k_A C_A + S_{mb} \tag{14.1.7.9.1.4}$$

where k_A is the method's sensitivity for the analyte and S_{mb} is the signal from the method blank. A ***method error*** exists when our value for k_A or for S_{mb} is in error. For example, a method in which S_{total} is the mass of a precipitate assumes that k is defined by a pure precipitate of known stoichiometry. If this assumption is not true, then the resulting determination of n_A or C_A is inaccurate. We can minimize a determinate error in k_A by calibrating the method. A method error due to an interferent in the reagents is minimized by using a proper method blank.

Measurement Errors

The manufacturers of analytical instruments and equipment, such as glassware and balances, usually provide a statement of the item's maximum ***measurement error***, or ***tolerance***. For example, a 10-mL volumetric pipet (Figure 3.2.1) has a tolerance of ±0.02 mL, which means the pipet delivers an actual volume within the range 9.98–10.02 mL at a temperature of 20 °C. Although we express this tolerance as a range, the error is determinate; that is, the pipet's expected volume, μ, is a fixed value within this stated range.

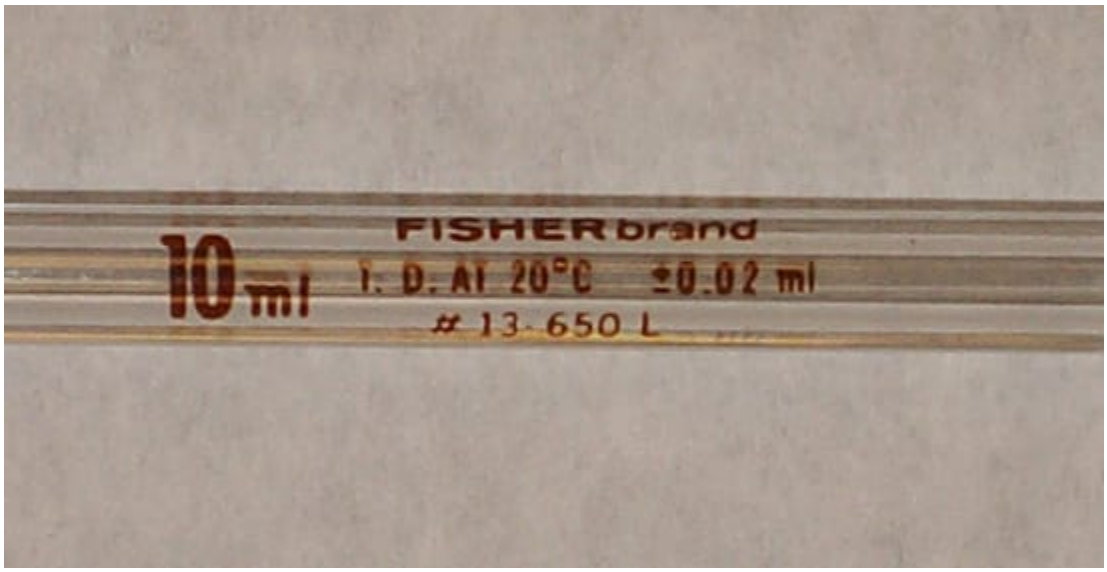


Figure 3.2.1 : Close-up of a 10-mL volumetric pipet showing that it has a tolerance of ±0.02 mL at 20 °C.

Volumetric glassware is categorized into classes based on its relative accuracy. **Class A glassware** is manufactured to comply with tolerances specified by an agency, such as the National Institute of Standards and Technology or the American Society for Testing and Materials. The tolerance level for Class A glassware is small enough that normally we can use it without calibration. The tolerance levels for **Class B glassware** usually are twice that for Class A glassware. In other words, Class B is less accurate. Other types of volumetric glassware, such as beakers and graduated cylinders, are not used to measure volume accurately. Table 3.2.1 provides a summary of typical measurement errors for Class A volumetric glassware. Tolerances for digital pipets and for balances are provided in Table 3.2.2 and Table 3.2.3 .

Tolerance Limits for Class A Volumetric Glassware

*Table 3.2.1 : Measurement Errors for **Class A Volumetric Glassware***

Volumetric Pipets		Volumetric Flasks		Burets	
Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)
1	± 0.006	5	± 0.02	10	± 0.02
2	± 0.006	10	± 0.02	25	± 0.03
5	± 0.01	25	± 0.03	50	± 0.05
10	± 0.02	50	± 0.05		
20	± 0.03	100	± 0.08		
25	± 0.03	250	± 0.12		
50	± 0.05	500	± 0.20		
100	± 0.08	1000	± 0.30		
		2000	± 0.50		

Tolerance limits for Digital Pipettes

Table 3.2.2 : Measurement Errors for Digital Pipets

Pipet Range	Volume (mL or μL)	Percent Measurement Error
10–100 μL	10	$\pm 3.0\%$
	50	$\pm 1.0\%$
	100	$\pm 0.8\%$
100–1000 μL	100	$\pm 3.0\%$
	500	$\pm 1.0\%$
	1000	$\pm 0.6\%$
1–10 mL	1	$\pm 3.0\%$
	5	$\pm 0.8\%$
	10	$\pm 0.6\%$

The tolerance values for the volumetric glassware in Table 3.2.1 are from the ASTM E288, E542, and E694 standards. The measurement errors for the digital pipets in Table 3.2.2 are from www.eppendorf.com.

Tolerance Limits for Some Common Balances

Table 3.2.3 : Measurement Errors for Selected Balances

Balance	Capacity (g)	Measurement Error
Precisa 160M	160	± 1 mg
A & D ER 120M	120	± 0.1 mg
Metler H54	160	± 0.01 mg

We can minimize a determinate measurement error by calibrating our equipment. Balances are calibrated using a reference

weight whose mass we can trace back to the SI standard kilogram. Volumetric glassware and digital pipets are calibrated by determining the mass of water delivered or contained and using the density of water to calculate the actual volume. It is never safe to assume that a calibration does not change during an analysis or over time. One study, for example, found that repeatedly exposing volumetric glassware to higher temperatures during machine washing and oven drying, led to small, but significant changes in the glassware's calibration [Castanheira, I.; Batista, E.; Valente, A.; Dias, G.; Mora, M.; Pinto, L.; Costa, H. S. *Food Control* **2006**, *17*, 719–726]. Many instruments drift out of calibration over time and may require frequent recalibration during an analysis.

Personal Errors

Finally, analytical work is always subject to ***personal error***, examples of which include the ability to see a change in the color of an indicator that signals the endpoint of a titration, biases, such as consistently overestimating or underestimating the value on an instrument's readout scale, failing to calibrate instrumentation, and misinterpreting procedural directions. You can minimize personal errors by taking proper care.

Identifying Determinate Errors

Determinate errors often are difficult to detect. Without knowing the expected value for an analysis, the usual situation in any analysis that matters, we often have nothing to which we can compare our experimental result. Nevertheless, there are strategies we can use to detect determinate errors.

The magnitude of a constant ***determinate error*** is the same for all samples and is more significant when we analyze smaller samples. Analyzing samples of different sizes, therefore, allows us to detect a constant determinate error. For example, consider a quantitative analysis in which we separate the analyte from its matrix and determine its mass. Let's assume the sample is 50.0% w/w analyte. As we see in Table 3.2.4 , the expected amount of analyte in a 0.100 g sample is 0.050 g. If the analysis has a positive constant determinate error of 0.010 g, then analyzing the sample gives 0.060 g of analyte, or an apparent concentration of 60.0% w/w. As we increase the size of the sample the experimental results become closer to the expected result. An upward or downward trend in a graph of the analyte's experimental concentration versus the sample's mass (Figure 3.2.2) is evidence of a constant determinate error.

Table 3.2.4 : Effect of a Constant Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Constant Error (g)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	0.010	0.060	60.0
0.200	0.100	0.010	0.110	55.0
0.400	0.200	0.010	0.210	52.5
0.800	0.400	0.010	0.410	51.2
1.600	0.800	0.010	0.810	50.6

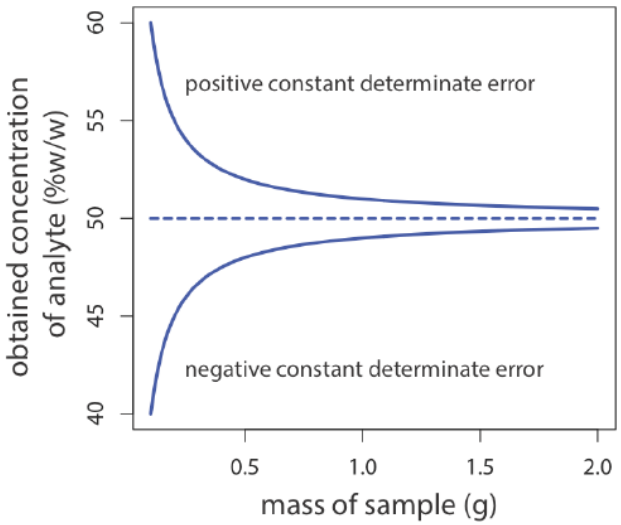


Figure 3.2.2 : Effect of a constant positive determinate error of +0.01 g and a constant negative determinate error of –0.01 g on the determination of an analyte in samples of varying size. The analyte's expected concentration of 50% w/w is shown by the dashed line.

A ***proportional determinate error***, in which the error's magnitude depends on the amount of sample, is more difficult to detect because the result of the analysis is independent of the amount of sample. Table 3.2.5 outlines an example that shows the effect of a positive proportional error of 1.0% on the analysis of a sample that is 50.0% w/w in analyte. Regardless of the sample's size, each analysis gives the same result of 50.5% w/w analyte.

Table 3.2.5 : Effect of a Proportional Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Proportional Error (%)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	1.00	0.0505	50.5
0.200	0.100	1.00	0.101	50.5
0.400	0.200	1.00	0.202	50.5
0.800	0.400	1.00	0.404	50.5
1.600	0.800	1.00	0.808	50.5

One approach for detecting a proportional determinate error is to analyze a standard that contains a known amount of analyte in a matrix similar to our samples. Standards are available from a variety of sources, such as the National Institute of Standards and Technology (where they are called Standard Reference Materials) or the American Society for Testing and Materials. Table 3.2.6 , for example, lists certified values for several analytes in a standard sample of *Gingko biloba* leaves. Another approach is to compare our analysis to an analysis carried out using an independent analytical method that is known to give accurate results. If the two methods give significantly different results, then a determinate error is the likely cause.

Table 3.2.6 : Certified Concentrations for SRM 3246: Gingko bilbo (Leaves)

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
Flavonoids/Ginkgolide B (mass fraction in mg/g)	Qurecetin	2.69 ± 0.31
	Kaempferol	3.02 ± 0.41
	Isorhamnetin	$0.517 \pm 0.0.99$
	Total Aglycones	6.22 ± 0.77
Selected Terpenes (mass fraction in mg/g)	Ginkgolide A	0.57 ± 0.28
	Ginkgolide B	0.470 ± 0.090

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
	Ginkgolide C	0.59 ± 0.22
	Ginkgolide J	0.18 ± 0.10
	Bilobalide	1.52 ± 0.40
	Total Terpene Lactones	3.3 ± 1.1
Selected Toxic Elements (mass fraction in ng/g)	Cadmium	20.8 ± 1.0
	Lead	995 ± 30
	Mercury	23.08 ± 0.17

The primary purpose of this Standard Reference Material is to validate analytical methods for determining flavonoids, terpene lactones, and toxic elements in *Ginkgo biloba* or other materials with a similar matrix. Values are from the official Certificate of Analysis available at www.nist.gov.

Constant and proportional determinate errors have distinctly different sources, which we can define in terms of the relationship between the signal and the moles or concentration of analyte (Equation 14.1.7.9.1.3 and Equation 14.1.7.9.1.4). An invalid method blank, S_{mb}, is a constant determinate error as it adds or subtracts the same value to the signal. A poorly calibrated method, which yields an invalid sensitivity for the analyte, k_A, results in a proportional determinate error.

Errors that Affect Precision

Precision is a measure of the spread of individual measurements or results about a central value, which we express as a range, a standard deviation, or a variance. Here we draw a distinction between two types of precision: repeatability and reproducibility. ***Repeatability*** is the precision when a single analyst completes an analysis in a single session using the same solutions, equipment, and instrumentation. ***Reproducibility***, on the other hand, is the precision under any other set of conditions, including between analysts or between laboratory sessions for a single analyst. Since reproducibility includes additional sources of variability, the reproducibility of an analysis cannot be better than its repeatability.

The ratio of the standard deviation associated with reproducibility to the standard deviation associated with repeatability is called the Horowitz ratio. For a wide variety of analytes in foods, for example, the median Horowtiz ratio is 2.0 with larger values for fatty acids and for trace elements; see Thompson, M.; Wood, R. "The 'Horowitz Ratio'–A Study of the Ratio Between Reproducibility and Repeatability in the Analysis of Foodstuffs," *Anal. Methods*, **2015**, *7*, 375–379.

Errors that affect precision are indeterminate and are characterized by random variations in their magnitude and their direction. Because they are random, positive and negative ***indeterminate errors*** tend to cancel, provided that we make a sufficient number of measurements. In such situations the mean and the median largely are unaffected by the precision of the analysis.

Sources of Indeterminate Error

We can assign indeterminate errors to several sources, including collecting samples, manipulating samples during the analysis, and making measurements. When we collect a sample, for instance, only a small portion of the available material is taken, which increases the chance that small-scale inhomogeneities in the sample will affect repeatability. Individual pennies, for example, may show variations in mass from several sources, including the manufacturing process and the loss of small amounts of metal or the addition of dirt during circulation. These variations are sources of indeterminate sampling errors.

During an analysis there are many opportunities to introduce indeterminate method errors. If our method for determining the mass of a penny includes directions for cleaning them of dirt, then we must be careful to treat each penny in the same way. Cleaning some pennies more vigorously than others might introduce an indeterminate method error.

Finally, all measuring devices are subject to indeterminate measurement errors due to limitations in our ability to read its scale. For example, a buret with scale divisions every 0.1 mL has an inherent indeterminate error of ±0.01–0.03 mL when we estimate the volume to the hundredth of a milliliter (Figure 3.2.3).

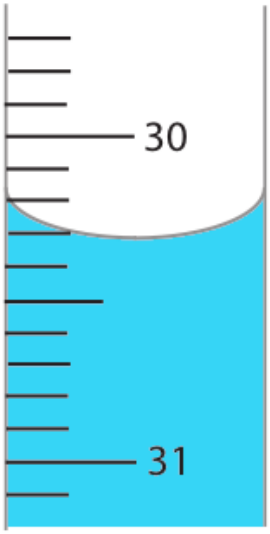


Figure 3.2.3 : Close-up of a buret showing the difficulty in estimating volume. With scale divisions every 0.1 mL it is difficult to read the actual volume to better than ±0.01–0.03 mL.

Evaluating Indeterminate Error

Indeterminate errors associated with our analytical equipment or instrumentation generally are easy to estimate if we measure the standard deviation for several replicate measurements, or if we monitor the signal's fluctuations over time in the absence of analyte (Figure 3.2.4) and calculate the standard deviation. Other sources of indeterminate error, such as treating samples inconsistently, are more difficult to estimate.

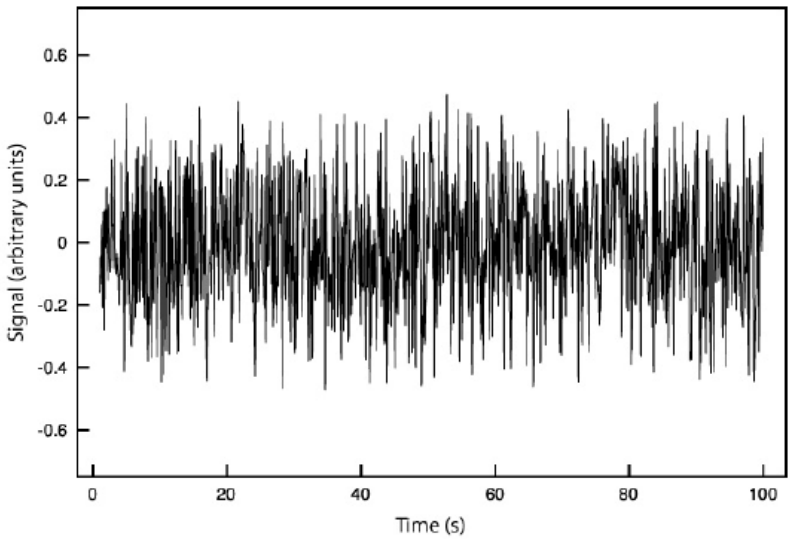


Figure 3.2.4 : Background noise in an instrument showing the random fluctuations in the signal.

Error and Uncertainty

Analytical chemists make a distinction between error and uncertainty [Ellison, S.; Wegscheider, W.; Williams, A. *Anal. Chem.* **1997**,

69, 607A–613A]. ***Error*** is the difference between a single measurement or result and its expected value. In other words, error is a measure of ***bias***. As discussed earlier, we divide errors into determinate and indeterminate sources. Although we can find and correct a source of determinate error, the indeterminate portion of the error remains.

Uncertainty expresses the range of possible values for a measurement or result. Note that this definition of uncertainty is not the same as our definition of precision. We calculate precision from our experimental data and use it to estimate the magnitude of indeterminate errors. Uncertainty accounts for all errors—both determinate and indeterminate—that reasonably might affect a measurement or a result. Although we always try to correct determinate errors before we begin an analysis, the correction itself is subject to uncertainty.

Here is an example to help illustrate the difference between precision and uncertainty. Suppose you purchase a 10-mL Class A pipet from a laboratory supply company and use it without any additional calibration. The pipet's tolerance of ±0.02 mL is its uncertainty because your best estimate of its expected volume is 10.00 mL ± 0.02 mL. This uncertainty primarily is determinate. If you use the pipet to dispense several replicate samples of a solution and determine the volume of each sample, the resulting standard deviation is the pipet's precision. Table 3.2.8 shows results for ten such trials, with a mean of 9.992 mL and a standard deviation of ±0.006 mL. This standard deviation is the precision with which we expect to deliver a solution using a Class A 10-mL pipet. In this case the pipet's published uncertainty of ±0.02 mL is worse than its experimentally determined precision of ±0.006 ml. Interestingly, the data in Table 3.2.8 allows us to calibrate this specific pipet's delivery volume as 9.992 mL. If we use this volume as a better estimate of the pipet's expected volume, then its uncertainty is ±0.006 mL. As expected, calibrating the pipet allows us to decrease its uncertainty [Kadis, R. *Talanta* **2004**, *64*, 167–173].

Table 3.2.8 : Experimental Results for Volume Dispensed by a 10–mL Class A Transfer Pipet

Replicate	Volume (ml)	Replicate	Volume (mL)
1	10.002	6	9.983
2	9.993	7	9.991
3	9.984	8	9.990
4	9.996	9	9.988
5	9.989	10	9.999

Adapted from 4.2: Characterizing Experimental Errors by David Harvey.

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14.1.7.9.2: Estimating and Reporting Error (Statistics, Propogation, and Rounding)

In many physical chemistry experiments, the goal is to obtain numerical results by taking measurements and calculating averages or applying theoretical formulas. However, simply producing a number isn't enough – it's essential to evaluate its quality. How accurate is the result? Accuracy indicates the level of uncertainty associated with the measurement. Overstating accuracy without proper justification can be misleading, while understating it can undervalue the result and lead to wasted effort and resources.

This page summarizes two main ways to approach the estimation of uncertainty. You will practice when and how to use each strategy by completing the problem set at the end of this module.

1. **Strategy 1: Statistical Analyses** can be used to estimate uncertainty when there are multiple replicates of the same measurement(s).
2. **Strategy 2: Propagation of Uncertainties** can be used to estimate uncertainty when using measured values in a function to calculate another numerical value (the vlaue of the function).

A major goal of this module is for you to learn when and how to apply these equations to perform statistical analysis or propagate uncertainties through a function. This skill will be required in nearly every future module in this course.

A summary of useful information and equations is below.

1. Statistical Analyses (on replicate measurements):

Average or mean: The average (or mean) of N measurements on the variable x is:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{14.1.7.9.2.1}$$

Standard deviation (S) is the spread around the mean of several replicate measurements. It has the same units as the measurement and is commonly used to report uncertainty (see Skoog Ch. 6 p 126)

$$S = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}} \tag{14.1.7.9.2.2}$$

Variance (S^2) is the dispersion between data points. The units are the square of the measured units.

The **Confidence Limits (CL)** are the values that define the confidence interval (which is the bounds about which an experimental value should be located with a given probability). The confidence limit is useful for small sample sizes. A common confidence limit is the 95% confidence limit, and its value is given by the following (see Skoog Ch7 pg 150 and Shoemaker Ch 2 eq 34).

$$CL_{0.95} = t_{0.95}S_m = t_{0.95}\frac{S}{\sqrt{N}} \tag{14.1.7.9.2.3}$$

or more generally

$$CL = \bar{x} \pm \frac{tS}{\sqrt{N}} \tag{14.1.7.9.2.4}$$

where t is the critical t value (from Student's t test) that depends on the degrees of freedom and the given probability. A table of critical t values can be found online. (See also Shoemaker Ch 2, Table 3)

2. Propagation of uncertainties (for values determined from a function):

Note on symbolism

I have chosen to use symbolism that is partly, but not completely, consistent with Shoemaker text. The following symbols are used on this page:

- **Values** are symbolized as x , y, z (these are values that have some uncertainty associated with them).
- The value of a **Function** is symbolized as F.
- **Uncertainty** in the values x, y, z, F are symbolized as u_x, u_y, u_z, u_F, respectively.*
- Coefficients or absolute constants are symbolized by a, b, c.

*u_x is used here to indicate the uncertainty in value x. Shoemaker uses $\Delta(x)$, which is a bit confusing, since it looks a lot like Δx which means "change in x" in many science fields. Ugh... u_x feels better to me, so I use it here.

Using partial derivatives

When using values (x , y, z) to calcuate the value of a function (F), we must propagate uncertainties of each operand (u_x, u_y, u_z,) to determine the uncertainty in the function's value u_F. This is accomplished by taking the square root of the sum of the squares of the partial derivative of the function with respect to each variable (eg partial derivative with respect to x is $\frac{\partial F}{\partial x}$), multiplied by the uncertainty in that variable (eg uncertainty in x is u_x, and the square of the uncertainty is u_x^2. In mathematical form, this is given below (from Shoemaker Ch 2 p 56, eq 54).

$$u_F^2 = \left(\frac{\partial F}{\partial x}\right)^2 u_x^2 + \left(\frac{\partial F}{\partial y}\right)^2 u_y^2 + \left(\frac{\partial F}{\partial z}\right)^2 u_z^2 + \ldots \tag{14.1.7.9.2.5}$$

It is convenient to rearrange this equation as follows to give the uncertainty in the value derived from the function:

$$u_F = \sqrt{\left(\frac{\partial F}{\partial x}\right)^2 u_x^2 + \left(\frac{\partial F}{\partial y}\right)^2 u_y^2 + \left(\frac{\partial F}{\partial z}\right)^2 u_z^2 + \ldots} \tag{14.1.7.9.2.6}$$

Simpler shortcuts:

In some cases, there are shortcuts that allow you to approximate uncertainties without taking the partial derivatives. In the examples below, assume that a, b, c are constants and x , y, z are variables with associated uncertaintyu_x, u_y, u_z:

For functions with only addition and subtraction of values with associated uncertainty (eg $F = ax \pm by \pm cz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 55)

$$u_F = \sqrt{a^2u_x^2 + b^2u_y^2 + c^2u_z^2} \tag{14.1.7.9.2.7}$$

For functions that involve only multiplication and division (eg $F = axyz$ **or** $F = axy/z$ **or** $F = a/xyz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 56)

$$u_F = F\sqrt{\frac{u_x^2}{x^2} + \frac{u_y^2}{y^2} + \frac{u_z^2}{z^2}} \tag{14.1.7.9.2.8}$$

For functions that involve taking a variable to the power of a constant (eg $F = ax^n$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 57)

$$u_F = F\sqrt{n^2\frac{u_x^2}{x^2}} \rightarrow u_F = Fn\frac{u_x}{x} \tag{14.1.7.9.2.9}$$

For functions where a variable is an exponent (eg $F = ae^x$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 58)

$$u_F = \sqrt{a^2e^{2x}u_x^2} \rightarrow u_F = Fu_x \tag{14.1.7.9.2.10}$$

For functions taking the logarithm of a variable (eg $F = a\ln(x)$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 59)

$$u_F = \sqrt{\frac{a^2}{x^2}u_x^2} \rightarrow u_F = a\frac{u_x}{x} \tag{14.1.7.9.2.11}$$

3. Reporting Numeric Results

All numeric results in this course should be reported with explicit statement of uncertainty. The following format is expected:

$$\text{Numeric Value } \pm \text{Uncertainty} \tag{14.1.7.9.2.12}$$

In your written assignments for this course use the following guidelines when reporting a "final" numeric value. You will be required to use your *best judgement* and to provide a *written justification* of your logic for reporting all final values. More detailed information is found below the guidelines and also in the Shoemaker text.

Guidelines for reporting final numerical values:

- Rules for reporting significant figures should be followed.
- The number of useful decimal places in the uncertainty should match the number of decimal places reported in the value.
- The certainty of a numeric value determined from a function cannot be be more than the certainty of its operands.

A summary of rules for reporting significant Figures (from Shoemaker Ch 2)

The following rules apply only for reporting the *final* value, not for intermediate rounding steps during calculation. In general, do not round values during the calculation process if it can be avoided. However, if you must round prior to completing a calculation, then retain *at least one digit more than would be considered "significant"*, and the more the better.

Rules for Rounding Final Values:

Follow the following rules depending on the digit immediately to the right of the place you are rounding. The examples below are rounding to the place underlined, and **the digit immediately to the right is bolded**.

a. Increase the last retained digit by 1 if the nearest dropped digit is more than 5, or if it is 5 followed by any non-zero digits:
   - Examples:
     6.78**9** rounds to 6.79
     54.9**1**23 rounds to 54.9
b. Leave the last retained digit unchanged if the nearest dropped digit is less than 5:
   - Examples:
     2.34**6** rounds to 2.35
     0.21**2**3 rounds to 0.21
c. If the leftmost digit to be dropped is 5 followed by no digits except zero, then increase the last retained digit by 1 if it is odd, and leave it unchanged if it is even:
   - Examples:
     15.32**5** rounds to 15.32
     15.33**5** rounds to 15.34
d. There are times when you should retain an extra digit so that your reported uncertainty is reasonable.

Rules for tracking significant figures for calculated values

Addition: When adding numeric values, the result's precision is limited by the least precise value involved. The number of decimal places in the result should match the fewest decimal places in any component. For example:

$$\begin{aligned} &15.4 \\ +&2.87 \\ +&7.621 \\ =&25.916 \rightarrow 25.9 \end{aligned} \tag{14.1.7.9.2.13}$$

Subtraction: When subtracting, the result's precision is limited by the least precise value involved, and the precision of the result will always be less than that of the operands. For example:

$$\begin{aligned} &289.461 \\ -&288.58 \\ &0.881 \rightarrow 0.88 \end{aligned} \tag{14.1.7.9.2.14}$$

Let's do an analysis to illustrate what this means. In the example above, let's assume an uncertainty of ± 3 in the rightmost digit of each number. Based on this assumption, the least precise operand has uncertainty of ~ 0.01%, while the final reported value has an uncertainty of 3.4%!

When multiplying and dividing: In multiplication and division, the precision of the result is limited by the least precise number involved. The number of significant figures in the result should align with the component having the fewest. ***Note that relative precision isn't solely dependent on the number of significant figures;*** for instance, 99 with two significant figures is approximately as precise as 101 with three. When unsure, do an analysis of the relative uncertainty, and if the uncertinties are approximately equal, use the larger number of significant figures.

Conventions for Reporting and Interpreting Reported Values

1. Numerical values are typically considered uncertain in the last digit by ±3 or more, with perhaps slight uncertainty in the next-to-last digit by up to ±2.
2. If the last digit to be retained is a one or two, an additional digit is retained so that precision is not inappropriately reported due to rounding.

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14.1.7.9.3: Least Squares Linear Regression

Your experimental data will usually be examined in graphic form, which can be more instructive than tabulated data. In any graphic presentation, be sure to plot your independent variable on the abscissa (x-axis) and the dependent variable on the ordinate (y-axis).

If the data are presented in graphic form, the usual procedure is to fit the best curve through the experimental points. As Brownlee[3] puts it,

> "When an investigator observes simultaneously two variables, x and y, usually with good reason he plots the observations on a graph. If there is any sign of an association, he is usually seized with the impulse to fit a line, usually a straight line or, rather infrequently, a parabola or cubic."

When we are "seized with the impulse" to fit a straight line curve the process of curve fitting is called linear regression. We assume that the deviations of the dependent variable y are distributed normally (that is, a Gaussian distribution). This assumption is not required for the determination of the least squares parameters, but it is necessary for construction of confidence intervals or for tests of hypotheses about the parameters. The parameters obtained by least squares under these conditions are unbiased and provide the best estimates of the curve fitting parameters.

Most of the experimental data that you will encounter this semester will have a simple functional form, or can be manipulated in such a way as to assume a simple form. We shall assume here that our data follows a linear relationship. For example, consider a gas that is thought to follow the equation of state

$$\begin{gathered} \mathrm{Z} \equiv \frac{\mathrm{PV}}{\mathrm{nRT}} = \mathrm{B}_0 + \mathrm{B}_1\mathrm{P} \\ \mathrm{y} = \mathrm{a} + \mathrm{bx} \end{gathered} \tag{14.1.7.9.3.1}$$

Measurements of Z, called the compressibility factor, are made at each of a series of pressures in an effort to determine B_0 andB_0. The least squares approach can be used to determine the slope (b, orB_1) and y-intercept (a, or B_0) which define the best straight line that can be drawn through the data. In simple linear regression analysis, it is assumed that all the error in the measurement lies in the dependent variable (y). This is equivalent to assuming that the precision of the determination of the independent variable (x) is considerable higher than that of y. The measured value of some quantity (y_i) will differ from the value predicted by a linear equation ($y = a + bx$) by an amount r_i called the residual.

$$r_i = y_i - a - bx \tag{14.1.7.9.3.2}$$

The least squares approach identifies the best straight line as the one for which R, the sum of the squares of the residuals, has the smallest value:

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} (y_i - a - bx_i)^2 \tag{14.1.7.9.3.3}$$

The arrows in Figure 4 represent the residuals, and all of them are equally weighted.

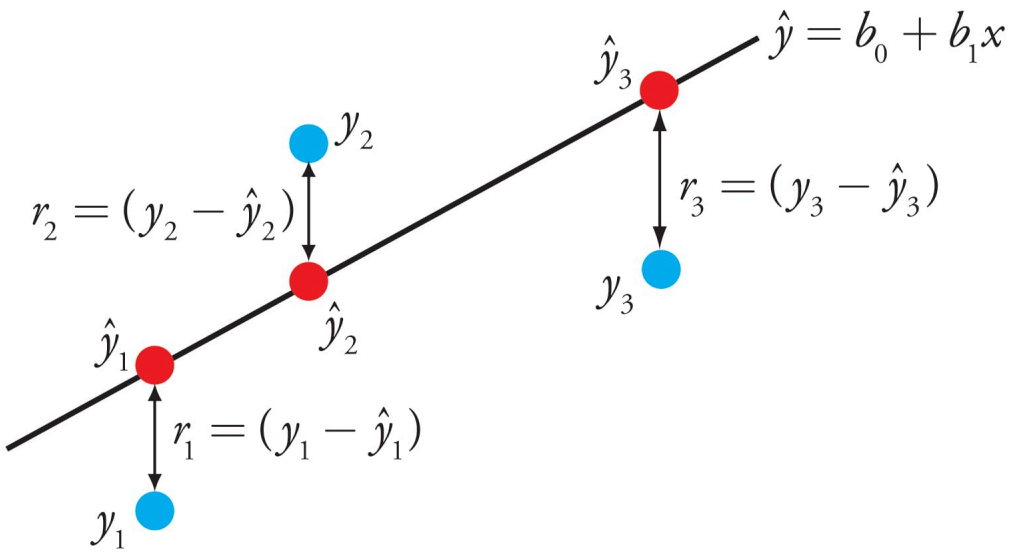


Figure 14.1.7.9.3.1: Least Squares Linear Regression: *Illustration showing the evaluation of a linear regression in which we assume that all uncertainty is the result of indeterminate errors affecting y. The points in blue, y_i, are the original data and the points in red, $\hat{y}_i$, are the predicted values from the regression equation, $\hat{y} = b_0 + b_1 x$. The smaller the total residual error, the better the fit of the straight-line to the data* (source)

We want to minimize the sum of the squares of the residuals. That is, we want to make *least* the sum of *squares* of residuals, and, thus, the name of the procedure. Since this is a minimization problem, we require that R be as small as possible with respect to a and b by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial a}\right)_b = -2\sum(y_i - a - bx_i) = 0 \tag{14.1.7.9.3.4}$$
$$\left(\frac{\partial R}{\partial b}\right)_a = -2\sum((y_i - a - bx_i)(x_i)) = 0$$

Solving equations 14.1.7.9.3.4 simultaneously, we obtain

$$a = \frac{(\sum x_i^2)(\sum y_i) - (\sum x_i)(\sum x_i y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{14.1.7.9.3.5}$$

$$b = \frac{N(\sum x_i y_i) - (\sum x_i)(\sum y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{14.1.7.9.3.6}$$

While we ultimately want to fit the data to $y_i = a + bx_i$ for a series i of N points, the theoretical development is much easier if we use $y_i = c + b(x_i - \overline{x})$ where obviously a and c are related by $a = c - b\overline{x}$, and where $\overline{x}$ is simply the mean of the x data, $n\overline{x} = \sum_{i=1}^{N} x_i$. This designation of variables is better because "it turns out" that in this approach the parameters b and c are independent, their variances are independent, and the formulas to transform to the parameters a and b are simple. Again, we want to minimize the sum of the squares of the residuals $r_i = y_i - c - b(x_i - \overline{x})$, R.

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} [y_i - (c + b(x_i - \overline{x}))]^2 \tag{14.1.7.9.3.7}$$

Now we require that R be as small as possible with respect to b and c by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial c}\right)_b = -2\sum (y_i - c - b\,(x_i - \overline{x})) = 0 \tag{14.1.7.9.3.8}$$
$$\left(\frac{\partial R}{\partial b}\right)_c = -2\sum ((y_i - c - b\,(x_i - \overline{x}))\,(x_i - \overline{x})) = 0$$

These two equations are readily rewritten as

$$\begin{aligned} \sum y_i &= \sum c + \sum b\left(x_i - \overline{x}\right) \\ \sum y_i\left(x_i - \overline{x}\right) &= \sum c\left(x_i - \overline{x}\right) + \sum b\left(x_i - \overline{x}\right)^2 \end{aligned} \tag{14.1.7.9.3.9}$$

which, since $\sum\left(x_i - \overline{x}\right) = 0$, simplify to

$$\begin{aligned} c &= \frac{\sum y_i}{N} = -\overline{y} \\ b &= \frac{\sum y_i\left(x_i - \overline{x}\right)}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{14.1.7.9.3.10}$$

The knowledge of c and b then allows us to determine the parameter, a, $a = c - b\overline{x} = \overline{y} - b\overline{x}$, a particularly simple relation.

The variance and standard deviation of N data points was introduced previously. The appropriate treatment of the parameters c and b in the least squares procedure results in

$$\begin{aligned} V[c] &= \frac{s^2}{N} \\ V[b] &= \frac{s^2}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{14.1.7.9.3.11}$$

where

$$s^2 = \frac{1}{N-2}\sum\left(y_i - c - b\left(x_i - \overline{x}\right)\right)^2 = \frac{1}{N-2}\sum\left(y_i - a - bx_i\right)^2 = \frac{R_{min}}{N-2} \tag{14.1.7.9.3.12}$$

Because c and b are independent quantities, it can be shown that

$$\begin{aligned} V[a] &= V[c] + \overline{x}^2 V[b] \\ &= \frac{s^2}{N} + \overline{x}^2\frac{s^2}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{14.1.7.9.3.13}$$

The standard deviations of a and b, σ_a and σ_b, are then obtained by taking the square roots of V[a] and V[b].

Another statistic that is sometimes used is the *correlation coefficient,* r. It is given by the expression

$$r = \frac{N\sum x_i y_i - \sum x_i \sum y_i}{\sqrt{\left(N\sum x_i^2 - \left(\sum x_i\right)^2\right)\left(N\sum y_i^2 - \left(\sum y_i\right)^2\right)}} \tag{14.1.7.9.3.14}$$

When the absolute value of r is close to unity the correlation between the y and x data is good, when it is close to zero the correlation is poor. Because the correlation coefficient is sometimes hard to interpret, it is usually better to work with the standard deviations of the regression parameters, σ_a and σ_b.

Linear regression is a powerful tool that takes the guesswork out of obtaining best fit information. However, like all mathematical tools, it must be used with caution. While the standard deviations and the correlation coefficient give indications of the goodness of the fit, there is no substitute for graphing the data and looking at the result. Since the errors are assumed to be random, the y_i values should be scattered about the best fit straight line in a random fashion. The residuals should likewise be either positive or negative (and sum to zero) without any pattern. If the data show a pattern of curvature, it is possible that the results do not conform to the linear model proposed. A linear regression is *not* valid in this case. You should also be alert to the effects of systematic errors, which may change the slope or the intercept without affecting the linearity of the data.

Linear regression of the type discussed above relies on a number of critical assumptions. Among the most important is that all the uncertainty in each of the y values is the same. If the form of the equation required to provide a linear relationship produces an independent variable that contains a significant uncertainty, the set of conditions that produced the minimum in the residuals of the line may not be the set that actually minimizes the uncertainty in the data. In this case, a "non-linear" least squared technique such as simplex is recommended.

Note

In this course, you can use the MatLab lsq.m script to perform least squares analysis. The equations given above are included in the lsq script.

Weighted Least Squares Analysis

When measurements of the dependent variable incur different uncertainties, a ***weighted*** least squares technique should be used. In this approach, each residual ri is divided by a factor proportional to its uncertainty ε_{y_i}. Then R, the sum of the squares of the residuals, becomes

$$R = \sum_{i=1}^{N} \frac{r_i^2}{\varepsilon_{y_i^2}} = \sum_{i=1}^{N} \frac{1}{\varepsilon_{y_i^2}} (y_i - a - bx_i)^2 \tag{14.1.7.9.3.15}$$

Using the same minimization techniques described above, the slope and intercept for weighted least squares become

$$a = \frac{\sum \frac{x_i^2}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2} \right)^2} \tag{14.1.7.9.3.16}$$

$$b = \frac{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2} \right)^2} \tag{14.1.7.9.3.17}$$

Weighted least squares has utility in a number of applications in the physical chemistry laboratory. One common situation arises when a linear equation requires the log of a measured quantity to be the dependent variable. Consider for example, the measurement of vapor pressure. Most pressure sensing devices will provide a constant error in the measurement of P. If the dependent variable to be plotted is lnP, however, its uncertainty is not constant but decreases as P increases. Thus,

$$\varepsilon_{lnP} = \frac{\partial lnP}{\partial P} \varepsilon_P = \frac{\varepsilon_P}{P} \tag{14.1.7.9.3.18}$$

An appropriate weighting factor in this case would be $\varepsilon_{y_i} = \frac{1}{P}$.

When you use Matlab for data analysis this semester, the command **lsq(x,y)** will be used for least squares analysis of x, y data, and the command **wtlsq(x,y)** will be used for weighted least squares analysis. In the latter case, you will be asked for a weighting factor, e. In either case, the program will output the least squares slope, y-intercept, correlation coefficient, standard deviation of the slope, and standard deviation of the intercept.

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14.1.7.9.4: Rejection of Outliers (Q-test)

In a set of collected data, there may be one or more values that deviate markedly from the trend of the others; in other words, there may be one or more data points that seem suspicious. If a measurement appears suspicious, we need evidence before deciding that it is statistically discordant with the rest of the data. One tool for doing this is the **Q-test**.

> **You should not reject a piece of data that seems suspect until you perform a Q-test**.

In a set of data of three to ten measurements, the Q-test can be performed on a single suspicious data point as follows:

$$Q_{exp} \equiv \frac{|\text{ (suspected outlier's value) } - \text{ (value closest to it) }|}{\text{(highest value) } - \text{ (lowest value)}} \tag{14.1.7.9.4.1}$$

The following table provides critical values for $Q_{critical}(\alpha, n)$, where:

- α is the probability of incorrectly rejecting the suspected outlier,
- n is the number of samples in the data set.

Table 14.1.7.9.4.1*: Critical Values for Dixon's Q-Test*

$\frac{\alpha \longrightarrow}{\text{no. of samples}\downarrow}$	$Q_{critical}$ $\alpha = 0.1$ **(90% confidence limit)**	$Q_{critical}$ $\alpha = 0.05$ **(95% confidence limit)**	$Q_{critical}$ $\alpha = 0.04$ **(96% confidence limit)**	$Q_{critical}$ $\alpha = 0.02$ **(98% confidence limit)**	$Q_{critical}$ $\alpha = 0.01$ **(99% confidence limit)**
n = 3	0.941	0.970	0.976	0.988	0.994
n = 4	0.765	0.829	0.846	0.889	0.926
n = 5	0.642	0.710	0.729	0.780	0.821
n = 6	0.560	0.625	0.644	0.698	0.740
n = 7	0.507	0.568	0.586	0.637	0.680
n = 8	0.468	0.526	0.543	0.590	0.634
n = 9	0.437	0.493	0.510	0.555	0.598
n = 10	0.412	0.466	0.483	0.527	0.568

The Q-test:

Compare the value of Q_{exp} from the equation above to the critical value of $Q_{critical}$.

- If $Q_{exp} \geq Q_{critical}$ then the suspect value can be rejected.
- If $Q_{exp} \leq Q_{critical}$,the value should be retained in the data set.

For additional information consult Rorabacher, D. B. "Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's 'Q' Parameter and Related Subrange Ratios at the 95% confidence Level," *Anal. Chem.* **1991**, *63*, 139–146. (see also http://chem-net.blogspot.com/2013/01...atistical.html)

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- 35.5: Critical Values for Dixon's Q-Test by David Harvey is licensed CC BY-NC-SA 4.0.

14.1.7.9.5: Guidelines for Recording and Reporting Data in your ELN

Always consider uncertainty during an experiment, record it in your ELN, and include it in all calculations and reporting. Do not leave the lab until you are sure that you have a valid strategy for determining errors in all final values.

1. **Uncertainty Awareness:**
   Before leaving the lab area, ensure you have a valid strategy for estimating uncertainties in all measured and calculated values.

2. **Estimating Uncertainty During Measurements:**

   - **Equipment Uncertainty**: Record uncertainties provided by equipment or manufacturers (e.g., balance deviation, pipette error). If unavailable, assume uncertainty is ±0.5 of the smallest measurable unit.
   - **Replicates**: For three or more measurements, calculate the standard deviation of the mean.
   - **Function-Based Values**: Perform propagation of error analysis.
   - **Least Squares Fitting**: Use errors from fitted parameters (e.g., slope or intercept) and propagate uncertainty if used in further calculations. Avoid linear regression if data deviates significantly from linearity.
   - **Consult Instructors**: Seek help for unclear sources of uncertainty.

3. **Propagation of Error:**
   Combine individual uncertainties to estimate the overall uncertainty of the final result. Use partial derivatives where necessary, and assume constants (e.g., RR) are error-free.

4. **Reporting Results:**

   - Include propagated uncertainty with each result.
   - Compare results with literature values using percent or absolute error.
   - Ensure significant figures reflect uncertainty and justify their use.

5. **Replicate Measurements:**

   - Report the mean and precision (e.g., standard deviation).
   - Use the Q-test to justify excluding outliers.

6. **Single Measurements:**

   - Estimate and report uncertainty (random or systematic).
   - Compare accuracy to expected values if available.

7. **Least Squares Fitting:**

   - Use weighted or non-weighted regression based on data.
   - Reject outliers only using the Q-test on residuals.
   - Propagate uncertainty from fitted parameters to calculated values.

8. **Qualitative Uncertainty:**

For variables with no clear quantitative uncertainty, discuss potential sources and their impact on results. Provide reasonable estimates and substantiate with evidence.

9. **Before Leaving the Lab:**
    - Confirm all uncertainties are documented.
    - Check for systematic errors (e.g., calibration issues).
    - Ensure thorough records of measured values and associated uncertainties.

By following these steps, you ensure your experimental results are accurate, reproducible, and clearly reported.

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14.1.7.9.6: References and Additional Reading

1. Shoemaker, D.P.; Garland, C.W.; Nibler, J.W. Experiments in Physical Chemistry, 6th Edition, McGraw-Hill, New York, NY, 1996, pp 27-89.

2. Bettelheim, F. A., Experimental Physical Chemistry, W.B. Saunders Co., Philadelphia, 1971, Chapter 2.

3. Brownlee, K. A., Statistical Theory and Methodology in Science and Engineering, 2nd Edition, John Wiley and Sons, Inc., New York, New York, 1965, pp 334-338.

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14.1.7.9.7: Pre-lab Assignment

📅 **Due:** The pre-lab assignment must be completed before 1:00 PM on your scheduled lab meeting day (see syllabus schedule).

🕒 **Time:** Two to three hours in class during our first meeting. Plus, plan 4.5 hours outside of class to complete the reading and to attempt the problems in this assignment.

🎯 **Purpose**: This pre-meeting assignment is designed to help you arrive to our next meeting prepared to discuss strategies for estimating uncertainty for different types of experimental results, and for correct reporting of values and their uncertainties. Prepare to participate in the lab meeting by presenting problems on the board, answering questions from your peers, and asking your own questions.

Pre-lab assignment

In preparation for the lab meeting on Error Analysis, please do the following*:

1. **Read this entire module.**
2. **Read D.P. Shoemaker, C.W. Garland and J.W. Nibler, Experiments in Physical Chemistry, 6th Ed., McGraw Hill Co. Inc., New York, 1996, Chapter 2.**
3. **Make a sincere attempt (does not mean you must be correct) for all seven problems** in the problem set; work should be done in a way that you can track your progress and submit your work in electronic form.
4. **Submit record of your work** for all seven problems on Canvas prior to the meeting. Your pre-lab work will be graded based on work shown and evidence of sincere attempt.

Note that the textbooks referenced in this module are available in the Perkins library, and on Canvas in pdf format (or Duke students click here).
We will meet in a classroom, thus lab attire is not necessary for this session.

*For our overachievers and those who want more, recommended additional reading includes: D.A. Skoog, D.M. West, F.J. Holler and S.R. Crouch, Analytical Chemistry: An Introduction, 7th Ed., Saunders College Publishing, New York, 2000, Chapters 5-7.

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14.1.7.9.8: Learning Objectives, Important Info

In many physical chemistry experiments, the goal is to obtain numerical results by taking measurements and calculating averages or applying theoretical formulas. However, simply producing a number isn't enough – it's essential to evaluate its quality. How accurate is the result? Accuracy indicates the level of uncertainty associated with the measurement. Overstating accuracy without proper justification can be misleading, while understating it can undervalue the result and lead to wasted effort and resources.

This page summarizes two main ways to approach the estimation of uncertainty. You will practice when and how to use each strategy by completing the problem set at the end of this module.

1. **Strategy 1: Statistical Analyses** can be used to estimate uncertainty when there are multiple replicates of the same measurement(s).
2. **Strategy 2: Propagation of Uncertainties** can be used to estimate uncertainty when using measured values in a function to calculate another numerical value (the vlaue of the function).

A major goal of this module is for you to learn when and how to apply these equations to perform statistical analysis or propagate uncertainties through a function. This skill will be required in nearly every future module in this course.

A summary of useful information and equations is below.

1. Statistical Analyses (on replicate measurements):

Average or mean: The average (or mean) of N measurements on the variable x is:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{14.1.7.9.8.1}$$

Standard deviation (S) is the spread around the mean of several replicate measurements. It has the same units as the measurement and is commonly used to report uncertainty (see Skoog Ch. 6 p 126)

$$S = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}} \tag{14.1.7.9.8.2}$$

Variance (S^2) is the dispersion between data points. The units are the square of the measured units.

The **Confidence Limits (CL)** are the values that define the confidence interval (which is the bounds about which an experimental value should be located with a given probability). The confidence limit is useful for small sample sizes. A common confidence limit is the 95% confidence limit, and its value is given by the following (see Skoog Ch7 pg 150 and Shoemaker Ch 2 eq 34).

$$CL_{0.95} = t_{0.95}S_m = t_{0.95}\frac{S}{\sqrt{N}} \tag{14.1.7.9.8.3}$$

or more generally

$$CL = \bar{x} \pm \frac{tS}{\sqrt{N}} \tag{14.1.7.9.8.4}$$

where t is the critical t value (from Student's t test) that depends on the degrees of freedom and the given probability. A table of critical t values can be found online. (See also Shoemaker Ch 2, Table 3)

2. Propagation of uncertainties (for values determined from a function):

Note on symbolism

I have chosen to use symbolism that is partly, but not completely, consistent with Shoemaker text. The following symbols are used on this page:

- **Values** are symbolized as x , y, z (these are values that have some uncertainty associated with them).
- The value of a **Function** is symbolized as F.
- **Uncertainty** in the values x, y, z, F are symbolized as u_x, u_y, u_z, u_F, respectively.*
- Coefficients or absolute constants are symbolized by a, b, c.

*u_x is used here to indicate the uncertainty in value x. Shoemaker uses $\Delta(x)$, which is a bit confusing, since it looks a lot like Δx which means "change in x" in many science fields. Ugh... u_x feels better to me, so I use it here.

Using partial derivatives

When using values (x , y, z) to calcuate the value of a function (F), we must propagate uncertainties of each operand (u_x, u_y, u_z,) to determine the uncertainty in the function's value u_F. This is accomplished by taking the square root of the sum of the squares of the partial derivative of the function with respect to each variable (eg partial derivative with respect to x is $\frac{\partial F}{\partial x}$), multiplied by the uncertainty in that variable (eg uncertainty in x is u_x, and the square of the uncertainty is u_x^2. In mathematical form, this is given below (from Shoemaker Ch 2 p 56, eq 54).

$$u_F^2 = \left(\frac{\partial F}{\partial x}\right)^2 u_x^2 + \left(\frac{\partial F}{\partial y}\right)^2 u_y^2 + \left(\frac{\partial F}{\partial z}\right)^2 u_z^2 + \ldots \tag{14.1.7.9.8.5}$$

It is convenient to rearrange this equation as follows to give the uncertainty in the value derived from the function:

$$u_F = \sqrt{\left(\frac{\partial F}{\partial x}\right)^2 u_x^2 + \left(\frac{\partial F}{\partial y}\right)^2 u_y^2 + \left(\frac{\partial F}{\partial z}\right)^2 u_z^2 + \ldots} \tag{14.1.7.9.8.6}$$

Simpler shortcuts:

In some cases, there are shortcuts that allow you to approximate uncertainties without taking the partial derivatives. In the examples below, assume that a, b, c are constants and x , y, z are variables with associated uncertaintyu_x, u_y, u_z:

For functions with only addition and subtraction of values with associated uncertainty (eg $F = ax \pm by \pm cz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 55)

$$u_F = \sqrt{a^2u_x^2 + b^2u_y^2 + c^2u_z^2} \tag{14.1.7.9.8.7}$$

For functions that involve only multiplication and division (eg $F = axyz$ **or** $F = axy/z$ **or** $F = a/xyz$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 56)

$$u_F = F\sqrt{\frac{u_x^2}{x^2} + \frac{u_y^2}{y^2} + \frac{u_z^2}{z^2}} \tag{14.1.7.9.8.8}$$

For functions that involve taking a variable to the power of a constant (eg $F = ax^n$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 57)

$$u_F = F\sqrt{n^2\frac{u_x^2}{x^2}} \rightarrow u_F = Fn\frac{u_x}{x} \tag{14.1.7.9.8.9}$$

For functions where a variable is an exponent (eg $F = ae^x$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 58)

$$u_F = \sqrt{a^2e^{2x}u_x^2} \rightarrow u_F = Fu_x \tag{14.1.7.9.8.10}$$

For functions taking the logarithm of a variable (eg $F = a\ln(x)$), we can use the following "shortcut": (Shoemaker, Ch 2, p 57, eq 59)

$$u_F = \sqrt{\frac{a^2}{x^2}u_x^2} \rightarrow u_F = a\frac{u_x}{x} \tag{14.1.7.9.8.11}$$

3. Reporting Numeric Results

All numeric results in this course should be reported with explicit statement of uncertainty. The following format is expected:

$$\text{Numeric Value } \pm \text{Uncertainty} \tag{14.1.7.9.8.12}$$

In your written assignments for this course use the following guidelines when reporting a "final" numeric value. You will be required to use your *best judgement* and to provide a *written justification* of your logic for reporting all final values. More detailed information is found below the guidelines and also in the Shoemaker text.

Guidelines for reporting final numerical values:

- Rules for reporting significant figures should be followed.
- The number of useful decimal places in the uncertainty should match the number of decimal places reported in the value.
- The certainty of a numeric value determined from a function cannot be be more than the certainty of its operands.

A summary of rules for reporting significant Figures (from Shoemaker Ch 2)

The following rules apply only for reporting the *final* value, not for intermediate rounding steps during calculation. In general, do not round values during the calculation process if it can be avoided. However, if you must round prior to completing a calculation, then retain *at least one digit more than would be considered "significant"*, and the more the better.

Rules for Rounding Final Values:

Follow the following rules depending on the digit immediately to the right of the place you are rounding. The examples below are rounding to the place underlined, and **the digit immediately to the right is bolded**.

a. Increase the last retained digit by 1 if the nearest dropped digit is more than 5, or if it is 5 followed by any non-zero digits:
   - Examples:
     6.78**9** rounds to 6.79
     54.91**2**3 rounds to 54.9
b. Leave the last retained digit unchanged if the nearest dropped digit is less than 5:
   - Examples:
     2.34**6** rounds to 2.35
     0.212**3** rounds to 0.21
c. If the leftmost digit to be dropped is 5 followed by no digits except zero, then increase the last retained digit by 1 if it is odd, and leave it unchanged if it is even:
   - Examples:
     15.32**5** rounds to 15.32
     15.33**5** rounds to 15.34
d. There are times when you should retain an extra digit so that your reported uncertainty is reasonable.

Rules for tracking significant figures for calculated values

Addition: When adding numeric values, the result's precision is limited by the least precise value involved. The number of decimal places in the result should match the fewest decimal places in any component. For example:

$$\begin{aligned} &15.4 \\ &+2.87 \\ &+7.621 \\ &=25.916 \rightarrow 25.9 \end{aligned} \tag{14.1.7.9.8.13}$$

Subtraction: When subtracting, the result's precision is limited by the least precise value involved, and the precision of the result will always be less than that of the operands. For example:

$$\begin{aligned} &289.461 \\ &-288.58 \\ &0.881 \rightarrow 0.88 \end{aligned} \tag{14.1.7.9.8.14}$$

Let's do an analysis to illustrate what this means. In the example above, let's assume an uncertainty of ± 3 in the rightmost digit of each number. Based on this assumption, the least precise operand has uncertainty of ~ 0.01%, while the final reported value has an uncertainty of 3.4%!

When multiplying and dividing: In multiplication and division, the precision of the result is limited by the least precise number involved. The number of significant figures in the result should align with the component having the fewest. ***Note that relative precision isn't solely dependent on the number of significant figures;*** for instance, 99 with two significant figures is approximately as precise as 101 with three. When unsure, do an analysis of the relative uncertainty, and if the uncertinties are approximately equal, use the larger number of significant figures.

Conventions for Reporting and Interpreting Reported Values

1. Numerical values are typically considered uncertain in the last digit by ±3 or more, with perhaps slight uncertainty in the next-to-last digit by up to ±2.
2. If the last digit to be retained is a one or two, an additional digit is retained so that precision is not inappropriately reported due to rounding.

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Guidelines

1. **Before you leave the lab, remember to do the following**:
   (a) Make note of the uncertainties in each of the physical quantities you measure. Follow the suggestions in step (2) below. Consult your TA concerning systematic errors that may arise from instrumental calibration and measurements.
   (b) Be aware of the consequences of systematic errors, such as starting the clock too late in one of the kinetics experiments.
2. **Some rules of thumb on estimation of uncertainties in mass, volume, pressure and temperature measurements**
   (a) Find and record the uncertainties associated with your equipment and instrumentation. This information is often listed right on the device, or is easily obtained from the manufactures statement of equipment specifications. In the rare event that such information is not available, you may assume that single experimentally measured values are uncertain in the last digit by at least ± 0.5 of the smallest unit or measurable digit. For example, if a digital voltmeter reads 5.432 V, and no other information is available, the uncertainty may be estimated to be ± 0.005 V.
   (b) The uncertainty of our analytical balances is either ± 0.0001 g or ± 0.0002 g, You can often find it stated on the individual balance and associated with the letter d (for deviation). For example, the label might say d=0.1 mg.
   (c) The position of the liquid level in a burette or a graduated 1 mL Mohr pipet can be estimated to ± 0.05 mL (half of the smallest unit measurable). Initial and final readings must be made, however, so that the probable error in the volume measured will be,

   $$\sqrt{(0.05)^2 + (0.05)^2} = 0.07 \tag{14.1.7.9.8.15}$$

   A similar analysis can be applied to pressure determination by measurement of mercury levels in a U-tube manometer.
   (d) For non-graduated volumetric pipets, the error limits can be found right on the pipet itself, or in the " Comparison of Class A and B Volumetric Glassware" link, found in the External Links section of your Sakai site or from other resources readily available online. You might also look in the Baxter Scientific catalog found in the lab. This catalog is a useful source for tolerances and error limits of thermometers, balances, pipets, burets, volumetric flasks and graduated cylinders.
3. **In the case of Replicate or Single Measurements**
   (a) If you make a series of replicate measurements of the same quantity, you should report the mean of that quantity together with its precision (standard deviation, variance or 95% confidence limits) calculated by statistical analysis. Unless otherwise

requested in the lab manual, use the standard deviation as a measure of precision. If the accepted value of the quantity has been reported in the literature, you might also report the percent error or absolute error as a measure of the accuracy of your measurement(s). If you feel that one of the replicate measurements should be rejected, use the Q-test to justify your decision.
(b) If you make a single measurement of a quantity, give your best estimate of the uncertainty in that measurement, whether random or systematic. If appropriate (see 2.2.3(a) above), you should also report the accuracy of that measurement. The suggestions given in Step (2.2.2) may help. Consult your TA if in doubt.

4. **Graphical Analysis**
   (a) If you use graphical analysis to determine the value of any quantity, you must make a decision whether or not to use a weighted least squares regression analysis. In most cases, a non-weighted analysis (using the command lsq in Matlab) will suffice. If you perform a weighted least squares analysis, you will have to decide on what weighting factor, e, to use. If the data deviate systematically from linearity, a linear regression analysis is meaningless, and should **not** be performed.
   (b) Outliers may be rejected only on the basis of a Q-test performed on the residuals.
   (c) The standard deviation may be used as a measure of the uncertainty in the slope and intercept calculated by linear least squares regression.
   (d) In most cases, you will use the values of the slope and/or y-intercept to calculate a physical quantity. In either case, you must perform a propagation of error treatment to determine the uncertainty in that physical quantity.
5. **Propagation of Error**
   Whether or not you perform a graphic analysis, you will use experimentally determined variables to calculate one or more physical quantities. In each case you must estimate the uncertainty in each measured variable and then propagate that uncertainty through to the final result. In a few simple cases you may take advantage of Equations (55) - (59) (Shoemaker et. al., 1996). Usually however, you will use Equation (54) (Shoemaker et. al., 1996), and take partial derivatives to calculate the probable propagated error. Physical constants, such as the gas constant, R, may be assumed to be error free.
6. **Reporting the Final Numerical Result(s) in your Notebooks and Reports**
   (a) Each numerical result should be reported together with the associated uncertainty, which is usually the probable propagated error. In addition, and where possible, you should report the accuracy of your result by comparison with literature values and calculation of the absolute error.
   (b) In reporting your results, ensure that the use of significant figures is appropriate to the uncertainty in those results. Use the conventions for significant figures and for rounding off data described earlier in this text.
7. **Discuss Qualitative Uncertainties in your Notebooks and Reports**
   In some cases, it may be difficult to quantitatively estimate the uncertainty in an experimental variable. In this instance, you may be asked to provide a qualitative discussion of the sources of uncertainty in the experiment. This discussion should be as thorough as possible. You should include "reasonable" estimates of the uncertainties in measured parameters together with a discussion of how these uncertainties will affect the final result. Any estimates of uncertainty should be substantiated by hard facts!!

And finally, if you read nothing else .....

1. Estimate the uncertainty in each experimentally determined variable. Usually this involves one or more of the following:

(a) Calculate the standard deviation of a quantity determined from the mean of a series of replicate measurements.

(b) Find and record the uncertainties associated with your equipment and instrumentation. This information is often listed right on the device, or is easily obtained from the manufactures statement of equipment specifications. In the rare event that such information is not available, you may assume that single experimentally measured values are uncertain in the last digit by at least ± 0.5 of the smallest unit or measurable digit. For example, if a digital voltmeter reads 5.432 V, and no other information is available, the uncertainty may be estimated to be ± 0.005 V.

(c) Perform a simple propagation of error analysis (usually equation (54) (Shoemaker et. al., 1996)) if a quantity (e.g., volume, pressure) is determined from a difference of two or more readings.

(d) Extraction of a Physical Quantity from Graphical Analysis: Calculation of the standard deviation of the slope (or intercept) is followed by a propagation of error treatment of the functional form of that slope (or intercept) to give the uncertainty in the physical quantity to be extracted. If the data deviate systematically from linearity, a linear regression analysis is meaningless and should not be performed.

(e) If the source or estimation of uncertainty seems more obscure, **-- CONSULT YOUR TA BEFORE YOU LEAVE THE LAB.**

2. Once you have determined the uncertainties associated with each individual measurement, perform a propagation of error treatment to estimate their combined effect on the uncertainty of the physical quantity of interest. Use equation (54) or some combination of equations (55) - (59) (Shoemaker et. al., 1996). Physical constants such as the Gas Constant, R, may be assumed to be error free.

3. Report your final result(s), the probable propagated error associated with that result, and the percent error or absolute error if appropriate literature values are available.

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14.1.7.9.9: Characterizing Experimental Errors (1)

In this course, you will need to determine the confidence in your results by doing appropriate error analysis. This section and the next are meant to review the types of experimental errors that affect accuracy and precision and to remind you of the simple methods for propagating error.

Errors That Affect Accuracy

Accuracy is how close a measure of central tendency is to its expected value, μ. We express accuracy either as an absolute error, *e*

$$e = \overline{X} - \mu \tag{14.1.7.9.9.1}$$

or as a percent relative error, %*e*

$$\%e = \frac{\overline{X} - \mu}{\mu} \times 100 \tag{14.1.7.9.9.2}$$

Although Equation 14.1.7.9.9.1 and Equation 14.1.7.9.9.2 use the mean as the measure of central tendency, we also can use the median.

> The convention for representing a statistical parameter is to use a Roman letter for a value calculated from experimental data, and a Greek letter for its corresponding expected value. For example, the experimentally determined mean is $\overline{X}$ and its underlying expected value is μ. Likewise, the experimental standard deviation is s and the underlying expected value is σ.

We identify as determinate an error that affects the accuracy of an analysis. Each source of a ***determinate error*** has a specific magnitude and sign. Some sources of determinate error are positive and others are negative, and some are larger in magnitude and others are smaller in magnitude. The cumulative effect of these determinate errors is a net positive or negative error in accuracy.

> It is possible, although unlikely, that the positive and negative determinate errors will offset each other, producing a result with no net error in accuracy.

We assign determinate errors into four categories—sampling errors, method errors, measurement errors, and personal errors—each of which we consider in this section.

Sampling Errors

A determinate sampling error occurs when our sampling strategy does not provide a us with a representative sample. For example, if we monitor the environmental quality of a lake by sampling from a single site near a point source of pollution, such as an outlet for industrial effluent, then our results will be misleading. To determine the mass of a U. S. penny, our strategy for selecting pennies must ensure that we do not include pennies from other countries.

> An awareness of potential sampling errors especially is important when we work with heterogeneous materials. Strategies for obtaining representative samples are covered in Chapter 5 of Harvey's Analytical Chemistry text on LibreTexts.

Method Errors

In any analysis the relationship between the signal, S_{total}, and the absolute amount of analyte, n_A, or the analyte's concentration, C_A, is

$$S_{total} = k_A n_A + S_{mb} \tag{14.1.7.9.9.3}$$

$$S_{total} = k_A C_A + S_{mb} \tag{14.1.7.9.9.4}$$

where k_A is the method's sensitivity for the analyte and S_{mb} is the signal from the method blank. A ***method error*** exists when our value for k_A or for S_{mb} is in error. For example, a method in which S_{total} is the mass of a precipitate assumes that k is defined by a pure precipitate of known stoichiometry. If this assumption is not true, then the resulting determination of n_A or C_A is inaccurate. We can minimize a determinate error in k_A by calibrating the method. A method error due to an interferent in the reagents is minimized by using a proper method blank.

Measurement Errors

The manufacturers of analytical instruments and equipment, such as glassware and balances, usually provide a statement of the item's maximum ***measurement error***, or ***tolerance***. For example, a 10-mL volumetric pipet (Figure 14.1.7.9.9.1) has a tolerance of ±0.02 mL, which means the pipet delivers an actual volume within the range 9.98–10.02 mL at a temperature of 20 °C. Although we express this tolerance as a range, the error is determinate; that is, the pipet's expected volume, μ, is a fixed value within this stated range.

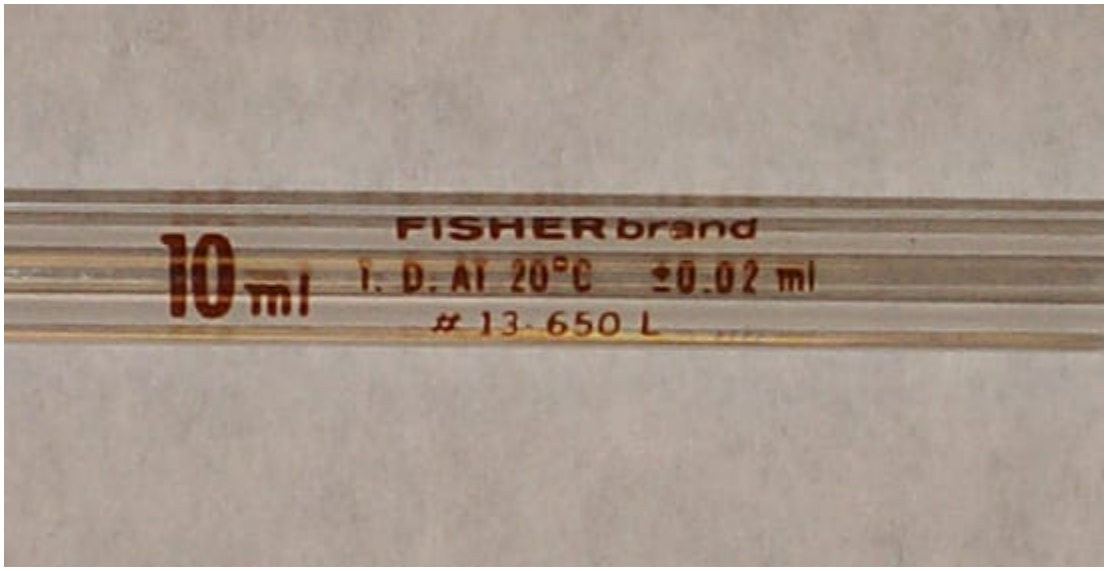


Figure 14.1.7.9.9.1 : Close-up of a 10-mL volumetric pipet showing that it has a tolerance of ±0.02 mL at 20 °C.

Volumetric glassware is categorized into classes based on its relative accuracy. **Class A glassware** is manufactured to comply with tolerances specified by an agency, such as the National Institute of Standards and Technology or the American Society for Testing and Materials. The tolerance level for Class A glassware is small enough that normally we can use it without calibration. The tolerance levels for **Class B glassware** usually are twice that for Class A glassware. In other words, Class B is less accurate. Other types of volumetric glassware, such as beakers and graduated cylinders, are not used to measure volume accurately. Table 14.1.7.9.9.1 provides a summary of typical measurement errors for Class A volumetric glassware. Tolerances for digital pipets and for balances are provided in Table 14.1.7.9.9.2 and Table 14.1.7.9.9.3 .

Tolerance Limits for Class A Volumetric Glassware

*Table 14.1.7.9.9.1 : Measurement Errors for **Class A Volumetric Glassware***

Volumetric Pipets		Volumetric Flasks		Burets	
Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)	Capacity (mL)	Tolerance (mL)
1	± 0.006	5	± 0.02	10	± 0.02
2	± 0.006	10	± 0.02	25	± 0.03
5	± 0.01	25	± 0.03	50	± 0.05
10	± 0.02	50	± 0.05		
20	± 0.03	100	± 0.08		
25	± 0.03	250	± 0.12		
50	± 0.05	500	± 0.20		
100	± 0.08	1000	± 0.30		
		2000	± 0.50		

Tolerance limits for Digital Pipettes

Table 14.1.7.9.9.2 : Measurement Errors for Digital Pipets

Pipet Range	Volume (mL or μL)	Percent Measurement Error
10–100 μL	10	$\pm 3.0\%$
	50	$\pm 1.0\%$
	100	$\pm 0.8\%$
100–1000 μL	100	$\pm 3.0\%$
	500	$\pm 1.0\%$
	1000	$\pm 0.6\%$
1–10 mL	1	$\pm 3.0\%$
	5	$\pm 0.8\%$
	10	$\pm 0.6\%$

The tolerance values for the volumetric glassware in Table 14.1.7.9.9.1 are from the ASTM E288, E542, and E694 standards. The measurement errors for the digital pipets in Table 14.1.7.9.9.2 are from www.eppendorf.com.

Tolerance Limits for Some Common Balances

Table 14.1.7.9.9.3 : Measurement Errors for Selected Balances

Balance	Capacity (g)	Measurement Error
Precisa 160M	160	± 1 mg
A & D ER 120M	120	± 0.1 mg
Metler H54	160	± 0.01 mg

We can minimize a determinate measurement error by calibrating our equipment. Balances are calibrated using a reference

weight whose mass we can trace back to the SI standard kilogram. Volumetric glassware and digital pipets are calibrated by determining the mass of water delivered or contained and using the density of water to calculate the actual volume. It is never safe to assume that a calibration does not change during an analysis or over time. One study, for example, found that repeatedly exposing volumetric glassware to higher temperatures during machine washing and oven drying, led to small, but significant changes in the glassware's calibration [Castanheira, I.; Batista, E.; Valente, A.; Dias, G.; Mora, M.; Pinto, L.; Costa, H. S. *Food Control* **2006**, *17*, 719–726]. Many instruments drift out of calibration over time and may require frequent recalibration during an analysis.

Personal Errors

Finally, analytical work is always subject to ***personal error***, examples of which include the ability to see a change in the color of an indicator that signals the endpoint of a titration, biases, such as consistently overestimating or underestimating the value on an instrument's readout scale, failing to calibrate instrumentation, and misinterpreting procedural directions. You can minimize personal errors by taking proper care.

Identifying Determinate Errors

Determinate errors often are difficult to detect. Without knowing the expected value for an analysis, the usual situation in any analysis that matters, we often have nothing to which we can compare our experimental result. Nevertheless, there are strategies we can use to detect determinate errors.

The magnitude of a constant ***determinate error*** is the same for all samples and is more significant when we analyze smaller samples. Analyzing samples of different sizes, therefore, allows us to detect a constant determinate error. For example, consider a quantitative analysis in which we separate the analyte from its matrix and determine its mass. Let's assume the sample is 50.0% w/w analyte. As we see in Table 14.1.7.9.9.4 , the expected amount of analyte in a 0.100 g sample is 0.050 g. If the analysis has a positive constant determinate error of 0.010 g, then analyzing the sample gives 0.060 g of analyte, or an apparent concentration of 60.0% w/w. As we increase the size of the sample the experimental results become closer to the expected result. An upward or downward trend in a graph of the analyte's experimental concentration versus the sample's mass (Figure 14.1.7.9.9.2) is evidence of a constant determinate error.

Table 14.1.7.9.9.4 : Effect of a Constant Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Constant Error (g)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	0.010	0.060	60.0
0.200	0.100	0.010	0.110	55.0
0.400	0.200	0.010	0.210	52.5
0.800	0.400	0.010	0.410	51.2
1.600	0.800	0.010	0.810	50.6

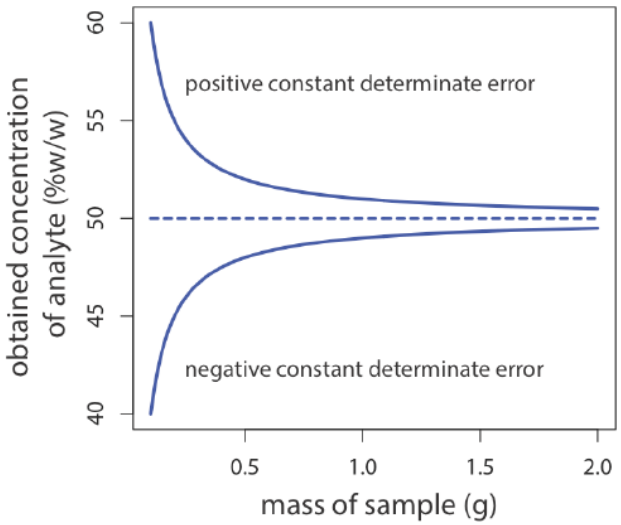


Figure 14.1.7.9.9.2 : Effect of a constant positive determinate error of +0.01 g and a constant negative determinate error of –0.01 g on the determination of an analyte in samples of varying size. The analyte's expected concentration of 50% w/w is shown by the dashed line.

A ***proportional determinate error***, in which the error's magnitude depends on the amount of sample, is more difficult to detect because the result of the analysis is independent of the amount of sample. Table 14.1.7.9.9.5 outlines an example that shows the effect of a positive proportional error of 1.0% on the analysis of a sample that is 50.0% w/w in analyte. Regardless of the sample's size, each analysis gives the same result of 50.5% w/w analyte.

Table 14.1.7.9.9.5 : Effect of a Proportional Determinate Error on the Analysis of a Sample That is 50.0% w/w Analyte

Mass of Sample (g)	Expected Mass of Analyte (g)	Proportional Error (%)	Experimental Mass of Analyte (g)	Experimental Concentration of Analyte (% w/w)
0.100	0.050	1.00	0.0505	50.5
0.200	0.100	1.00	0.101	50.5
0.400	0.200	1.00	0.202	50.5
0.800	0.400	1.00	0.404	50.5
1.600	0.800	1.00	0.808	50.5

One approach for detecting a proportional determinate error is to analyze a standard that contains a known amount of analyte in a matrix similar to our samples. Standards are available from a variety of sources, such as the National Institute of Standards and Technology (where they are called Standard Reference Materials) or the American Society for Testing and Materials. Table 14.1.7.9.9.6 , for example, lists certified values for several analytes in a standard sample of *Gingko biloba* leaves. Another approach is to compare our analysis to an analysis carried out using an independent analytical method that is known to give accurate results. If the two methods give significantly different results, then a determinate error is the likely cause.

Table 14.1.7.9.9.6 : Certified Concentrations for SRM 3246: Gingko bilbo (Leaves)

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
Flavonoids/Ginkgolide B (mass fraction in mg/g)	Qurecetin	2.69 ± 0.31
	Kaempferol	3.02 ± 0.41
	Isorhamnetin	$0.517 \pm 0.0.99$
	Total Aglycones	6.22 ± 0.77
Selected Terpenes (mass fraction in mg/g)	Ginkgolide A	0.57 ± 0.28
	Ginkgolide B	0.470 ± 0.090

Class of Analyte	Analyte	Mass Fraction (mg/g or ng/g)
	Ginkgolide C	0.59 ± 0.22
	Ginkgolide J	0.18 ± 0.10
	Bilobalide	1.52 ± 0.40
	Total Terpene Lactones	3.3 ± 1.1
Selected Toxic Elements (mass fraction in ng/g)	Cadmium	20.8 ± 1.0
	Lead	995 ± 30
	Mercury	23.08 ± 0.17

> The primary purpose of this Standard Reference Material is to validate analytical methods for determining flavonoids, terpene lactones, and toxic elements in *Ginkgo biloba* or other materials with a similar matrix. Values are from the official Certificate of Analysis available at www.nist.gov.

Constant and proportional determinate errors have distinctly different sources, which we can define in terms of the relationship between the signal and the moles or concentration of analyte (Equation 14.1.7.9.9.3 and Equation 14.1.7.9.9.4). An invalid method blank, S_{mb}, is a constant determinate error as it adds or subtracts the same value to the signal. A poorly calibrated method, which yields an invalid sensitivity for the analyte, k_A, results in a proportional determinate error.

Errors that Affect Precision

Precision is a measure of the spread of individual measurements or results about a central value, which we express as a range, a standard deviation, or a variance. Here we draw a distinction between two types of precision: repeatability and reproducibility. ***Repeatability*** is the precision when a single analyst completes an analysis in a single session using the same solutions, equipment, and instrumentation. ***Reproducibility***, on the other hand, is the precision under any other set of conditions, including between analysts or between laboratory sessions for a single analyst. Since reproducibility includes additional sources of variability, the reproducibility of an analysis cannot be better than its repeatability.

> The ratio of the standard deviation associated with reproducibility to the standard deviation associated with repeatability is called the Horowitz ratio. For a wide variety of analytes in foods, for example, the median Horowtiz ratio is 2.0 with larger values for fatty acids and for trace elements; see Thompson, M.; Wood, R. "The 'Horowitz Ratio'–A Study of the Ratio Between Reproducibility and Repeatability in the Analysis of Foodstuffs," *Anal. Methods*, **2015**, *7*, 375–379.

Errors that affect precision are indeterminate and are characterized by random variations in their magnitude and their direction. Because they are random, positive and negative ***indeterminate errors*** tend to cancel, provided that we make a sufficient number of measurements. In such situations the mean and the median largely are unaffected by the precision of the analysis.

Sources of Indeterminate Error

We can assign indeterminate errors to several sources, including collecting samples, manipulating samples during the analysis, and making measurements. When we collect a sample, for instance, only a small portion of the available material is taken, which increases the chance that small-scale inhomogeneities in the sample will affect repeatability. Individual pennies, for example, may show variations in mass from several sources, including the manufacturing process and the loss of small amounts of metal or the addition of dirt during circulation. These variations are sources of indeterminate sampling errors.

During an analysis there are many opportunities to introduce indeterminate method errors. If our method for determining the mass of a penny includes directions for cleaning them of dirt, then we must be careful to treat each penny in the same way. Cleaning some pennies more vigorously than others might introduce an indeterminate method error.

Finally, all measuring devices are subject to indeterminate measurement errors due to limitations in our ability to read its scale. For example, a buret with scale divisions every 0.1 mL has an inherent indeterminate error of ±0.01–0.03 mL when we estimate the volume to the hundredth of a milliliter (Figure 14.1.7.9.9.3).

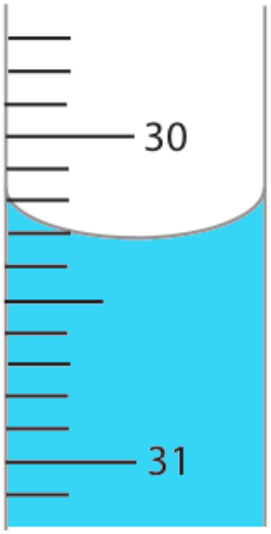


Figure 14.1.7.9.9.3 : Close-up of a buret showing the difficulty in estimating volume. With scale divisions every 0.1 mL it is difficult to read the actual volume to better than ±0.01–0.03 mL.

Evaluating Indeterminate Error

Indeterminate errors associated with our analytical equipment or instrumentation generally are easy to estimate if we measure the standard deviation for several replicate measurements, or if we monitor the signal's fluctuations over time in the absence of analyte (Figure 14.1.7.9.9.4) and calculate the standard deviation. Other sources of indeterminate error, such as treating samples inconsistently, are more difficult to estimate.

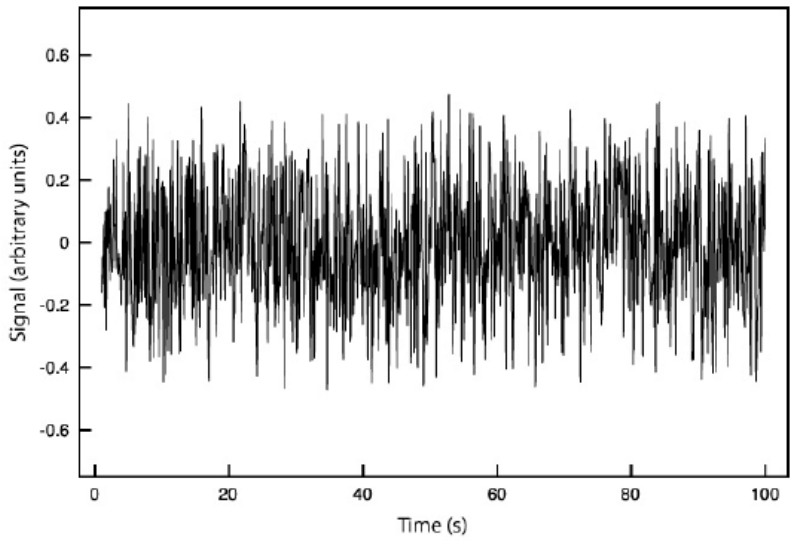


Figure 14.1.7.9.9.4 : Background noise in an instrument showing the random fluctuations in the signal.

Error and Uncertainty

Analytical chemists make a distinction between error and uncertainty [Ellison, S.; Wegscheider, W.; Williams, A. *Anal. Chem.* **1997**,

69, 607A–613A]. ***Error*** is the difference between a single measurement or result and its expected value. In other words, error is a measure of ***bias***. As discussed earlier, we divide errors into determinate and indeterminate sources. Although we can find and correct a source of determinate error, the indeterminate portion of the error remains.

Uncertainty expresses the range of possible values for a measurement or result. Note that this definition of uncertainty is not the same as our definition of precision. We calculate precision from our experimental data and use it to estimate the magnitude of indeterminate errors. Uncertainty accounts for all errors—both determinate and indeterminate—that reasonably might affect a measurement or a result. Although we always try to correct determinate errors before we begin an analysis, the correction itself is subject to uncertainty.

Here is an example to help illustrate the difference between precision and uncertainty. Suppose you purchase a 10-mL Class A pipet from a laboratory supply company and use it without any additional calibration. The pipet's tolerance of ±0.02 mL is its uncertainty because your best estimate of its expected volume is 10.00 mL ± 0.02 mL. This uncertainty primarily is determinate. If you use the pipet to dispense several replicate samples of a solution and determine the volume of each sample, the resulting standard deviation is the pipet's precision. Table 14.1.7.9.9.8 shows results for ten such trials, with a mean of 9.992 mL and a standard deviation of ±0.006 mL. This standard deviation is the precision with which we expect to deliver a solution using a Class A 10-mL pipet. In this case the pipet's published uncertainty of ±0.02 mL is worse than its experimentally determined precision of ±0.006 ml. Interestingly, the data in Table 14.1.7.9.9.8 allows us to calibrate this specific pipet's delivery volume as 9.992 mL. If we use this volume as a better estimate of the pipet's expected volume, then its uncertainty is ±0.006 mL. As expected, calibrating the pipet allows us to decrease its uncertainty [Kadis, R. *Talanta* **2004**, *64*, 167–173].

Table 14.1.7.9.9.8 : Experimental Results for Volume Dispensed by a 10-mL Class A Transfer Pipet

Replicate	Volume (ml)	Replicate	Volume (mL)
1	10.002	6	9.983
2	9.993	7	9.991
3	9.984	8	9.990
4	9.996	9	9.988
5	9.989	10	9.999

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14.1.7.9.10: Propagation of Uncertainty

Suppose we dispense 20 mL of a reagent using the Class A 10-mL pipet whose calibration information is given in the Table in the previous section. If the volume and uncertainty for one use of the pipet is 9.992 ± 0.006 mL, what is the volume and uncertainty if we use the pipet twice?

As a first guess, we might simply add together the volume and the maximum uncertainty for each delivery; thus

$$(9.992\ \text{mL} + 9.992\ \text{mL}) \pm (0.006\ \text{mL} + 0.006\ \text{mL}) = 19.984 \pm 0.012\ \text{mL}$$

It is easy to appreciate that combining uncertainties in this way overestimates the total uncertainty. Adding the uncertainty for the first delivery to that of the second delivery assumes that with each use the indeterminate error is in the same direction and is as large as possible. At the other extreme, we might assume that the uncertainty for one delivery is positive and the other is negative. If we subtract the maximum uncertainties for each delivery,

$$(9.992\ \text{mL} + 9.992\ \text{mL}) \pm (0.006\ \text{mL} - 0.006\ \text{mL}) = 19.984 \pm 0.000\ \text{mL}$$

we clearly underestimate the total uncertainty.

So what is the total uncertainty? From the discussion above, we reasonably expect that the total uncertainty is greater than ±0.000 mL and that it is less than ±0.012 mL. To estimate the uncertainty we use a mathematical technique known as the propagation of uncertainty. Our treatment of the propagation of uncertainty is based on a few simple rules.

A Few Symbols

A ***propagation of uncertainty*** allows us to estimate the uncertainty in a result from the uncertainties in the measurements used to calculate that result. For the equations in this section we represent the result with the symbol *R*, and we represent the measurements with the symbols *A*, *B*, and *C*. The corresponding uncertainties are u_R, u_A, u_B, and u_C. We can define the uncertainties for *A*, *B*, and *C* using standard deviations, ranges, or tolerances (or any other measure of uncertainty), as long as we use the same form for all measurements.

> The requirement that we express each uncertainty in the same way is a critically important point. Suppose you have a range for one measurement, such as a pipet's tolerance, and standard deviations for the other measurements. All is not lost. There are ways to convert a range to an estimate of the standard deviation. See Appendix 2 of Harvey's Analytical Chemistry Text for more details.

Uncertainty When Adding or Subtracting

When we add or subtract measurements we propagate their absolute uncertainties. For example, if the result is given by the equation

$$R = A + B - C$$

the the absolute uncertainty in *R* is

$$u_R = \sqrt{u_A^2 + u_B^2 + u_C^2} \qquad (14.1.7.9.10.1)$$

Example 14.1.7.9.10.1

If we dispense 20 mL using a 10-mL Class A pipet, what is the total volume dispensed and what is the uncertainty in this volume? First, complete the calculation using the manufacturer's tolerance of 10.00 mL±0.02 mL, and then using the calibration data from the Table 1.3.8 in the previous section.

Solution

To calculate the total volume we add the volumes for each use of the pipet. When using the manufacturer's values, the total volume is

$$V = 10.00\ \text{mL} + 10.00\ \text{mL} = 20.00\ \text{mL}$$

and when using the calibration data, the total volume is

$$V = 9.992\ \text{mL} + 9.992\ \text{mL} = 19.984\ \text{mL}$$

Using the pipet's tolerance as an estimate of its uncertainty gives the uncertainty in the total volume as

$$u_R = (0.02)^2 + (0.02)^2 = 0.028\ \text{mL} = 0.028\ \text{mL}$$

and using the standard deviation for the data in Table 1.3.8 gives an uncertainty of

$$u_R = (0.006)^2 + (0.006)^2 = 0.0085\ \text{mL}$$

Rounding the volumes to four significant figures gives 20.00 mL ± 0.03 mL when we use the tolerance values, and 19.98 ± 0.01 mL when we use the calibration data.

Uncertainty When Multiplying or Dividing

When we multiple or divide measurements we propagate their relative uncertainties. For example, if the result is given by the equation

$$R = \frac{A \times B}{C}$$

then the relative uncertainty in *R* is

$$\frac{u_R}{R} = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2 + \left(\frac{u_C}{C}\right)^2} \qquad (14.1.7.9.10.2)$$

Example 14.1.7.9.10.2

The quantity of charge, Q, in coulombs that passes through an electrical circuit is

$$Q = i \times t$$

where *i* is the current in amperes and *t* is the time in seconds. When a current of 0.15 A ± 0.01 A passes through the circuit for 120 s ± 1 s, what is the total charge and its uncertainty?

Solution

The total charge is

$$Q = (0.15\ \text{A}) \times (120\ \text{s}) = 18\ \text{C}$$

Since charge is the product of current and time, the relative uncertainty in the charge is

$$u_R = \sqrt{\left(\frac{0.01}{0.15}\right)^2 + \left(\frac{1}{120}\right)^2} = 0.0672$$

and the charge's absolute uncertainty is

$$u_R = R \times 0.0672 = (18\text{ C}) \times (0.0672) = 1.2\text{ C}$$

Thus, we report the total charge as 18 C ± 1 C.

Uncertainty for Mixed Operations

Many chemical calculations involve a combination of adding and subtracting, and of multiply and dividing. As shown in the following example, we can calculate the uncertainty by separately treating each operation using Equation 14.1.7.9.10.1 and Equation 14.1.7.9.10.2 as needed.

Example 14.1.7.9.10.3

For a concentration technique, the relationship between the signal and the an analyte's concentration is

$$S_{total} = k_A C_A + S_{mb}$$

What is the analyte's concentration, C_A, and its uncertainty if S_{total} is 24.37 ± 0.02, S_{mb} is 0.96 ± 0.02, and k_A is $0.186 \pm 0.003\text{ ppm}^{-1}$?

Solution

Rearranging the equation and solving for C_A

$$C_A = \frac{S_{total} - S_{mb}}{k_A} = \frac{24.37 - 0.96}{0.186\text{ ppm}^{-1}} = \frac{23.41}{0.186\text{ ppm}^{-1}} = 125.9\text{ ppm}$$

gives the analyte's concentration as 126 ppm. To estimate the uncertainty in C_A, we first use Equation 14.1.7.9.10.1 to determine the uncertainty for the numerator.

$$u_R = \sqrt{(0.02)^2 + (0.02)^2} = 0.028$$

The numerator, therefore, is 23.41 ± 0.028. To complete the calculation we use Equation 14.1.7.9.10.2 to estimate the relative uncertainty in C_A.

$$\frac{u_R}{R} = \sqrt{\left(\frac{0.028}{23.41}\right)^2 + \left(\frac{0.003}{0.186}\right)^2} = 0.0162$$

The absolute uncertainty in the analyte's concentration is

$$u_R = (125.9\text{ ppm}) \times (0.0162) = 2.0\text{ ppm}$$

Thus, we report the analyte's concentration as 126 ppm ± 2 ppm.

Exercise 14.1.7.9.10.1

To prepare a standard solution of Cu^{2+} you obtain a piece of copper from a spool of wire. The spool's initial weight is 74.2991 g and its final weight is 73.3216 g. You place the sample of wire in a 500-mL volumetric flask, dissolve it in 10 mL of HNO_3, and dilute to volume. Next, you pipet a 1 mL portion to a 250-mL volumetric flask and dilute to volume. What is the final concentration of Cu^{2+} in mg/L, and its uncertainty? Assume that the uncertainty in the balance is ±0.1 mg and that you are using Class A glassware.

Answer available at the end of this section.

Uncertainty for Other Mathematical Functions

Many other mathematical operations are common in analytical chemistry, including the use of powers, roots, and logarithms. Table 14.1.7.9.10.1 provides equations for propagating uncertainty for some of these function where *A* and *B* are independent measurements and where *k* is a constant whose value has no uncertainty.

Table 14.1.7.9.10.1 : Propagation of Uncertainty for Selected Mathematical Functions

Function	u_R	Function	u_R
$R = kA$	$u_R = ku_A$	$R = \ln(A)$	$u_R = \frac{u_A}{A}$
$R = A + B$	$u_R = \sqrt{u_A^2 + u_B^2}$	$R = \log(A)$	$u_R = 0.4343 \times \frac{u_A}{A}$
$R = A - B$	$u_R = \sqrt{u_A^2 + u_B^2}$	$R = e^A$	$\frac{u_R}{R} = u_A$
$R = A \times B$	$u_R = \sqrt{(\frac{u_A}{A})^2 + (\frac{u_B}{B})^2}$	$R = 10^A$	$\frac{u_R}{R} = 2.303 \times u_A$
$R = \frac{A}{B}$	$u_R = \sqrt{(\frac{u_A}{A})^2 + (\frac{u_B}{B})^2}$	$R = A^k$	$\frac{u_R}{R} = k \times \frac{u_A}{A}$

Example 14.1.7.9.10.4

If the pH of a solution is 3.72 with an absolute uncertainty of ±0.03, what is the $[H^+]$ and its uncertainty?

Solution

The concentration of H^+ is

$$[\mathrm{H^+}] = 10^{-\mathrm{pH}} = 10^{-3.72} = 1.91 \times 10^{-4}\ \mathrm{M}$$

or 1.9×10^{-4} M to two significant figures. From Table 14.1.7.9.10.1 the relative uncertainty in $[H^+]$ is

$$\frac{u_R}{R} = 2.303 \times u_A = 2.303 \times 0.03 = 0.069$$

The uncertainty in the concentration, therefore, is

$$(1.91 \times 10^{-4}\ \mathrm{M}) \times (0.069) = 1.3 \times 10^{-5}\ \mathrm{M}$$

We report the $[H^+]$ as $1.9(\pm 0.1) \times 10^{-4}$ M, which is equivalent to $1.9 \times 10^{-4}\ \mathrm{M}\ \pm 0.1 \times 10^{-4}\ \mathrm{M}$.

Exercise 14.1.7.9.10.2

A solution of copper ions is blue because it absorbs yellow and orange light. Absorbance, *A*, is defined as

$$A = -\log T = -\log\left(\frac{P}{P_o}\right)$$

where, *T* is the transmittance, P_o is the power of radiation as emitted from the light source and *P* is its power after it passes through the solution. What is the absorbance if P_o is 3.80×10^2 and *P* is 1.50×10^2? If the uncertainty in measuring P_o and *P* is 15, what is the uncertainty in the absorbance?

Answer available at the end of this section.

Is Calculating Uncertainty Actually Useful?

Given the effort it takes to calculate uncertainty, it is worth asking whether such calculations are useful. The short answer is, yes. Let's consider three examples of how we can use a propagation of uncertainty to help guide the development of an analytical method.

One reason to complete a propagation of uncertainty is that we can compare our estimate of the uncertainty to that obtained experimentally. For example, to determine the mass of a penny we measure its mass twice—once to tare the balance at 0.000 g and once to measure the penny's mass. If the uncertainty in each measurement of mass is ±0.001 g, then we estimate the total uncertainty in the penny's mass as

$$u_R = \sqrt{(0.001)^2 + (0.001)^2} = 0.0014 \text{ g}$$

If we measure a single penny's mass several times and obtain a standard deviation of ±0.050 g, then we have evidence that the measurement process is out of control. Knowing this, we can identify and correct the problem.

We also can use a propagation of uncertainty to help us decide how to improve an analytical method's uncertainty. In Example 14.1.7.9.10.3 , for instance, we calculated an analyte's concentration as 126 ppm ± 2 ppm, which is a percent uncertainty of 1.6%. Suppose we want to decrease the percent uncertainty to no more than 0.8%. How might we accomplish this? Looking back at the calculation, we see that the concentration's relative uncertainty is determined by the relative uncertainty in the measured signal (corrected for the reagent blank)

$$\frac{0.028}{23.41} = 0.0012 \text{ or } 0.12\%$$

and the relative uncertainty in the method's sensitivity, k_A,

$$\frac{0.003 \text{ ppm}^{-1}}{0.186 \text{ ppm}^{-1}} = 0.016 \text{ or } 1.6\%$$

Of these two terms, the uncertainty in the method's sensitivity dominates the overall uncertainty. Improving the signal's uncertainty will not improve the overall uncertainty of the analysis. To achieve an overall uncertainty of 0.8% we must improve the uncertainty in k_A to ±0.0015 ppm^{-1}.

Exercise 14.1.7.9.10.3

Verify that an uncertainty of ±0.0015 ppm^{-1} for k_A is the correct result.

Answer available at the end of this section.

Finally, we can use a propagation of uncertainty to determine which of several procedures provides the smallest uncertainty.

When we dilute a stock solution usually there are several combinations of volumetric glassware that will give the same final concentration. For instance, we can dilute a stock solution by a factor of 10 using a 10-mL pipet and a 100-mL volumetric flask, or using a 25-mL pipet and a 250-mL volumetric flask. We also can accomplish the same dilution in two steps using a 50-mL pipet and 100-mL volumetric flask for the first dilution, and a 10-mL pipet and a 50-mL volumetric flask for the second dilution. The overall uncertainty in the final concentration—and, therefore, the best option for the dilution—depends on the uncertainty of the volumetric pipets and volumetric flasks. As shown in the following example, we can use the tolerance values for volumetric glassware to determine the optimum dilution strategy [Lam, R. B.; Isenhour, T. L. *Anal. Chem.* **1980**, *52*, 1158–1161].

Example 14.1.7.9.10.5 :

Which of the following methods for preparing a 0.0010 M solution from a 1.0 M stock solution provides the smallest overall uncertainty?

(a) A one-step dilution that uses a 1-mL pipet and a 1000-mL volumetric flask.

(b) A two-step dilution that uses a 20-mL pipet and a 1000-mL volumetric flask for the first dilution, and a 25-mL pipet and a 500-mL volumetric flask for the second dilution.

Solution

The dilution calculations for case (a) and case (b) are

$$\text{case (a): } 1.0 \text{ M} \times \frac{1.000 \text{ mL}}{1000.0 \text{ mL}} = 0.0010 \text{ M}$$

$$\text{case (b): } 1.0 \text{ M} \times \frac{20.00 \text{ mL}}{1000.0 \text{ mL}} \times \frac{25.00 \text{ mL}}{500.0 \text{mL}} = 0.0010 \text{ M}$$

Using tolerance values from Table 2.1.3.1, the relative uncertainty for case (a) is

$$u_R = \sqrt{\left(\frac{0.006}{1.000}\right)^2 + \left(\frac{0.3}{1000.0}\right)^2} = 0.006$$

and for case (b) the relative uncertainty is

$$u_R = \sqrt{\left(\frac{0.03}{20.00}\right)^2 + \left(\frac{0.3}{1000}\right)^2 + \left(\frac{0.03}{25.00}\right)^2 + \left(\frac{0.2}{500.0}\right)^2} = 0.002$$

Since the relative uncertainty for case (b) is less than that for case (a), the two-step dilution provides the smallest overall uncertainty. Of course we must balance the smaller uncertainty for case (b) against the increased opportunity for introducing a determinate error when making two dilutions instead of just one dilution, as in case (a).

Answers

The first step is to determine the concentration of Cu^{2+} in the final solution. The mass of copper is

$$74.2991 \text{ g} - 73.3216 \text{ g} = 0.9775 \text{ g Cu}$$

The 10 mL of HNO_3 used to dissolve the copper does not factor into our calculation. The concentration of Cu^{2+} is

$$\frac{0.9775 \text{ g Cu}}{0.5000 \text{ L}} \times \frac{1.000 \text{ mL}}{250.0 \text{ mL}} \times \frac{1000 \text{ mg}}{\text{g}} = 7.820 \text{ mg [redacted]/L}$$

Having found the concentration of Cu^{2+}, we continue with the propagation of uncertainty. The absolute uncertainty in the mass of Cu wire is

$$u_{\text{g Cu}} = \sqrt{(0.0001)^2 + (0.0001)^2} = 0.00014 \text{ g}$$

The relative uncertainty in the concentration of Cu^{2+} is

$$\frac{u_{\text{mg/L}}}{7.820 \text{ mg/L}} = \sqrt{\left(\frac{0.00014}{0.9775}\right)^2 + \left(\frac{0.20}{500.0}\right)^2 + \left(\frac{0.006}{1.000}\right)^2 + \left(\frac{0.12}{250.0}\right)^2} = 0.00603$$

Solving for $u_{\text{mg/L}}$ gives the uncertainty as 0.0472. The concentration and uncertainty for Cu^{2+} is 7.820 mg/L ± 0.047 mg/L.

The first step is to calculate the absorbance, which is

$$A = -\log T = -\log \frac{P}{P_o} = -\log \frac{1.50 \times 10^2}{3.80 \times 10^2} = 0.4037 \approx 0.404$$

Having found the absorbance, we continue with the propagation of uncertainty. First, we find the uncertainty for the ratio P/P_o, which is the transmittance, T.

$$\frac{u_T}{T} = \sqrt{\left(\frac{15}{3.80 \times 10^2}\right)^2 + \left(\frac{15}{1.50 \times 10^2}\right)^2} = 0.1075$$

Finally, from Table 14.1.7.9.10.1 the uncertainty in the absorbance is

$$u_A = 0.4343 \times \frac{u_T}{T} = (0.4343) \times (0.1075) = 4.669 \times 10^{-2}$$

The absorbance and uncertainty is 0.40 ± 0.05 absorbance units.

An uncertainty of 0.8% is a relative uncertainty in the concentration of 0.008; thus, letting u be the uncertainty in k_A

$$0.008 = \sqrt{\left(\frac{0.028}{23.41}\right)^2 + \left(\frac{u}{0.186}\right)^2}$$

Squaring both sides of the equation gives

$$6.4 \times 10^{-5} = \left(\frac{0.028}{23.41}\right)^2 + \left(\frac{u}{0.186}\right)^2$$

Solving for the uncertainty in k_A gives its value as 1.47×10^{-3} or ±0.0015 ppm^{-1}.

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- 4.3: Propagation of Uncertainty by David Harvey is licensed CC BY-NC-SA 4.0.

14.1.7.9.11: LEAST SQUARES LINEAR REGRESSION (1)

Your experimental data will usually be examined in graphic form, which can be more instructive than tabulated data. In any graphic presentation, be sure to plot your independent variable on the abscissa (x-axis) and the dependent variable on the ordinate (y-axis).

If the data are presented in graphic form, the usual procedure is to fit the best curve through the experimental points. As Brownlee[3] puts it,

> "When an investigator observes simultaneously two variables, x and y, usually with good reason he plots the observations on a graph. If there is any sign of an association, he is usually seized with the impulse to fit a line, usually a straight line or, rather infrequently, a parabola or cubic."

When we are "seized with the impulse" to fit a straight line curve the process of curve fitting is called linear regression. We assume that the deviations of the dependent variable y are distributed normally (that is, a Gaussian distribution). This assumption is not required for the determination of the least squares parameters, but it is necessary for construction of confidence intervals or for tests of hypotheses about the parameters. The parameters obtained by least squares under these conditions are unbiased and provide the best estimates of the curve fitting parameters.

Most of the experimental data that you will encounter this semester will have a simple functional form, or can be manipulated in such a way as to assume a simple form. We shall assume here that our data follows a linear relationship. For example, consider a gas that is thought to follow the equation of state

$$\begin{gathered} \mathrm{Z} \equiv \frac{\mathrm{PV}}{\mathrm{nRT}} = \mathrm{B}_0 + \mathrm{B}_1\mathrm{P} \\ \mathrm{y} = \mathrm{a} + \mathrm{bx} \end{gathered} \tag{14.1.7.9.11.1}$$

Measurements of Z, called the compressibility factor, are made at each of a series of pressures in an effort to determine B_0 andB_0. The least squares approach can be used to determine the slope (b, orB_1) and y-intercept (a, or B_0) which define the best straight line that can be drawn through the data. In simple linear regression analysis, it is assumed that all the error in the measurement lies in the dependent variable (y). This is equivalent to assuming that the precision of the determination of the independent variable (x) is considerable higher than that of y. The measured value of some quantity (y_i) will differ from the value predicted by a linear equation ($y = a + bx$) by an amount r_i called the residual.

$$r_i = y_i - a - bx \tag{14.1.7.9.11.2}$$

The least squares approach identifies the best straight line as the one for which R, the sum of the squares of the residuals, has the smallest value:

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} (y_i - a - bx_i)^2 \tag{14.1.7.9.11.3}$$

The arrows in Figure 4 represent the residuals, and all of them are equally weighted.

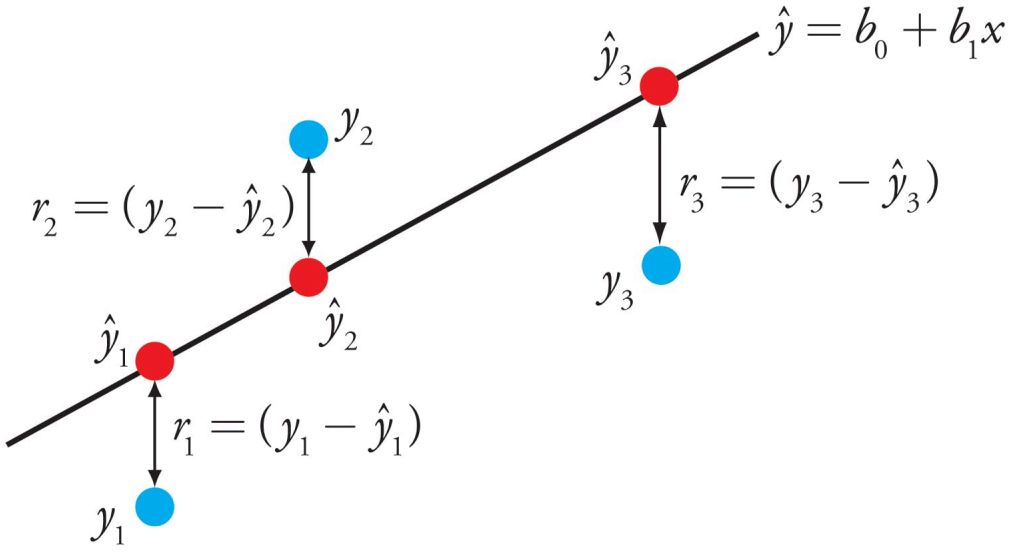


Figure 14.1.7.9.11.1: Least Squares Linear Regression: *Illustration showing the evaluation of a linear regression in which we assume that all uncertainty is the result of indeterminate errors affecting y. The points in blue, y_i, are the original data and the points in red, $\hat{y}_i$, are the predicted values from the regression equation, $\hat{y} = b_0 + b_1 x$. The smaller the total residual error, the better the fit of the straight-line to the data* (source)

We want to minimize the sum of the squares of the residuals. That is, we want to make *least* the sum of *squares* of residuals, and, thus, the name of the procedure. Since this is a minimization problem, we require that R be as small as possible with respect to a and b by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial a}\right)_b = -2\sum(y_i - a - bx_i) = 0 \tag{14.1.7.9.11.4}$$
$$\left(\frac{\partial R}{\partial b}\right)_a = -2\sum((y_i - a - bx_i)(x_i)) = 0$$

Solving equations 14.1.7.9.11.4 simultaneously, we obtain

$$a = \frac{(\sum x_i^2)(\sum y_i) - (\sum x_i)(\sum x_i y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{14.1.7.9.11.5}$$

$$b = \frac{N(\sum x_i y_i) - (\sum x_i)(\sum y_i)}{N(\sum x_i^2) - (\sum x_i)^2} \tag{14.1.7.9.11.6}$$

While we ultimately want to fit the data to $y_i = a + bx_i$ for a series i of N points, the theoretical development is much easier if we use $y_i = c + b(x_i - \overline{x})$ where obviously a and c are related by $a = c - b\overline{x}$, and where $\overline{x}$ is simply the mean of the x data, $n\overline{x} = \sum_{i=1}^{N} x_i$. This designation of variables is better because "it turns out" that in this approach the parameters b and c are independent, their variances are independent, and the formulas to transform to the parameters a and b are simple. Again, we want to minimize the sum of the squares of the residuals $r_i = y_i - c - b(x_i - \overline{x})$, R.

$$R = \sum_{i=1}^{N} r_i^2 = \sum_{i=1}^{N} [y_i - (c + b(x_i - \overline{x}))]^2 \tag{14.1.7.9.11.7}$$

Now we require that R be as small as possible with respect to b and c by taking derivatives with respect to these two parameters and setting the derivatives equal to zero.

$$\left(\frac{\partial R}{\partial c}\right)_b = -2\sum (y_i - c - b\,(x_i - \overline{x})) = 0 \tag{14.1.7.9.11.8}$$
$$\left(\frac{\partial R}{\partial b}\right)_c = -2\sum ((y_i - c - b\,(x_i - \overline{x}))\,(x_i - \overline{x})) = 0$$

These two equations are readily rewritten as

$$\begin{aligned} \sum y_i &= \sum c + \sum b\left(x_i - \overline{x}\right) \\ \sum y_i\left(x_i - \overline{x}\right) &= \sum c\left(x_i - \overline{x}\right) + \sum b\left(x_i - \overline{x}\right)^2 \end{aligned} \tag{14.1.7.9.11.9}$$

which, since $\sum\left(x_i - \overline{x}\right) = 0$, simplify to

$$\begin{aligned} c &= \frac{\sum y_i}{N} = -\overline{y} \\ b &= \frac{\sum y_i\left(x_i - \overline{x}\right)}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{14.1.7.9.11.10}$$

The knowledge of c and b then allows us to determine the parameter, a, $a = c - b\overline{x} = \overline{y} - b\overline{x}$, a particularly simple relation.

The variance and standard deviation of N data points was introduced previously. The appropriate treatment of the parameters c and b in the least squares procedure results in

$$\begin{aligned} V[c] &= \frac{s^2}{N} \\ V[b] &= \frac{s^2}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{14.1.7.9.11.11}$$

where

$$s^2 = \frac{1}{N-2}\sum\left(y_i - c - b\left(x_i - \overline{x}\right)\right)^2 = \frac{1}{N-2}\sum\left(y_i - a - bx_i\right)^2 = \frac{R_{min}}{N-2} \tag{14.1.7.9.11.12}$$

Because c and b are independent quantities, it can be shown that

$$\begin{aligned} V[a] &= V[c] + \overline{x}^2 V[b] \\ &= \frac{s^2}{N} + \overline{x}^2\frac{s^2}{\sum\left(x_i - \overline{x}\right)^2} \end{aligned} \tag{14.1.7.9.11.13}$$

The standard deviations of a and b, σ_a and σ_b, are then obtained by taking the square roots of V[a] and V[b].

Another statistic that is sometimes used is the *correlation coefficient,* r. It is given by the expression

$$r = \frac{N\sum x_i y_i - \sum x_i \sum y_i}{\sqrt{\left(N\sum x_i^2 - \left(\sum x_i\right)^2\right)\left(N\sum y_i^2 - \left(\sum y_i\right)^2\right)}} \tag{14.1.7.9.11.14}$$

When the absolute value of r is close to unity the correlation between the y and x data is good, when it is close to zero the correlation is poor. Because the correlation coefficient is sometimes hard to interpret, it is usually better to work with the standard deviations of the regression parameters, σ_a and σ_b.

Linear regression is a powerful tool that takes the guesswork out of obtaining best fit information. However, like all mathematical tools, it must be used with caution. While the standard deviations and the correlation coefficient give indications of the goodness of the fit, there is no substitute for graphing the data and looking at the result. Since the errors are assumed to be random, the y_i values should be scattered about the best fit straight line in a random fashion. The residuals should likewise be either positive or negative (and sum to zero) without any pattern. If the data show a pattern of curvature, it is possible that the results do not conform to the linear model proposed. A linear regression is *not* valid in this case. You should also be alert to the effects of systematic errors, which may change the slope or the intercept without affecting the linearity of the data.

Linear regression of the type discussed above relies on a number of critical assumptions. Among the most important is that all the uncertainty in each of the y values is the same. If the form of the equation required to provide a linear relationship produces an independent variable that contains a significant uncertainty, the set of conditions that produced the minimum in the residuals of the line may not be the set that actually minimizes the uncertainty in the data. In this case, a "non-linear" least squared technique such as simplex is recommended.

Note

In this course, you can use the MatLab lsq.m script to perform least squares analysis. The equations given above are included in the lsq script.

14.1.7.9.11.1: Rejection of Discordant Data

14.1.7.9.11.2: Weighted Least Squares Analysis

14.1.7.9.11.3: References

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14.1.7.9.11.1: Rejection of Discordant Data

In a set of collected data, there may be one or more values that deviate markedly from the trend of the others. You should not reject a piece of data that seems suspect until you perform a Q-test. In a set of data of three to ten measurements, the Q-test can be performed on the suspect data point:

$$Q_{exp} \equiv \frac{|\text{ (suspected outlier's value) } - \text{(value closest to it) }|}{\text{(highest value) } - \text{ (lowest value)}} \tag{14.1.7.9.11.1.1}$$

Compare the value of Q_{exp} from the equation above to the critical value of Q_r. If Q_{exp} is greater or equal to Q_r then the suspect value can be rejected. If Q_{exp} is less than Q_r,the value should be retained in the data set.

The following table provides critical values for $Q(\alpha, n)$, where α is the probability of incorrectly rejecting the suspected outlier and n is the number of samples in the data set. There are several versions of the Q-Test, each of which calculates a value for Q_{ij} where *i* is the number of suspected outliers on one end of the data set and *j* is the number of suspected outliers on the opposite end of the data set. The critical values for Q here are for a single outlier, Q_{10}, where

$$Q_{\text{exp}} = Q_{10} = \frac{|\text{ (suspected outlier's value) } - \text{(value closest to it) }|}{\text{(highest value) } - \text{ (lowest value)}}$$

The suspected outlier is rejected if Q_{exp} is greater than $Q(\alpha, n)$. For additional information consult Rorabacher, D. B. "Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's 'Q' Parameter and Related Subrange Ratios at the 95% confidence Level," *Anal. Chem.* **1991**, *63*, 139–146.

Table 14.1.7.9.11.1.1*: Critical Values for Dixon's Q-Test*

$\frac{\alpha\longrightarrow}{n\downarrow}$	**0.1 (90% confidence limit)**	**0.05 (95% confidence limit)**	**0.04 (96% confidence limit)**	**0.02 (98% confidence limit)**	**0.01 (99% confidence limit)**
3	0.941	0.970	0.976	0.988	0.994
4	0.765	0.829	0.846	0.889	0.926
5	0.642	0.710	0.729	0.780	0.821
6	0.560	0.625	0.644	0.698	0.740
7	0.507	0.568	0.586	0.637	0.680
8	0.468	0.526	0.543	0.590	0.634
9	0.437	0.493	0.510	0.555	0.598
10	0.412	0.466	0.483	0.527	0.568

(see also http://chem-net.blogspot.com/2013/01...atistical.html)

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- 35.5: Critical Values for Dixon's Q-Test by David Harvey is licensed CC BY-NC-SA 4.0.

14.1.7.9.11.2: Weighted Least Squares Analysis

When measurements of the dependent variable incur different uncertainties, a ***weighted*** least squares technique should be used. In this approach, each residual ri is divided by a factor proportional to its uncertainty ε_{y_i}. Then R, the sum of the squares of the residuals, becomes

$$R = \sum_{i=1}^{N} \frac{r_i^2}{\varepsilon_{y_i^2}} = \sum_{i=1}^{N} \frac{1}{\varepsilon_{y_i^2}} (y_i - a - bx_i)^2 \tag{14.1.7.9.11.2.1}$$

Using the same minimization techniques described above, the slope and intercept for weighted least squares become

$$a = \frac{\sum \frac{x_i^2}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2} \right)^2} \tag{14.1.7.9.11.2.2}$$

$$b = \frac{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i y_i}{\varepsilon_{y_i}^2} - \sum \frac{x_i}{\varepsilon_{y_i}^2} \sum \frac{y_i}{\varepsilon_{y_i}^2}}{\sum \frac{1}{\varepsilon_{y_i}^2} \sum \frac{x_i^2}{\varepsilon_{y_i}^2} - \left(\sum \frac{x_i}{\varepsilon_{y_i}^2} \right)^2} \tag{14.1.7.9.11.2.3}$$

Weighted least squares has utility in a number of applications in the physical chemistry laboratory. One common situation arises when a linear equation requires the log of a measured quantity to be the dependent variable. Consider for example, the measurement of vapor pressure. Most pressure sensing devices will provide a constant error in the measurement of P. If the dependent variable to be plotted is lnP, however, its uncertainty is not constant but decreases as P increases. Thus,

$$\varepsilon_{lnP} = \frac{\partial lnP}{\partial P} \varepsilon_P = \frac{\varepsilon_P}{P} \tag{14.1.7.9.11.2.4}$$

An appropriate weighting factor in this case would be $\varepsilon_{y_i} = \frac{1}{P}$.

When you use Matlab for data analysis this semester, the command **lsq(x,y)** will be used for least squares analysis of x, y data, and the command **wtlsq(x,y)** will be used for weighted least squares analysis. In the latter case, you will be asked for a weighting factor, e. In either case, the program will output the least squares slope, y-intercept, correlation coefficient, standard deviation of the slope, and standard deviation of the intercept.

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14.1.7.9.11.3: References

1. Shoemaker, D.P.; Garland, C.W.; Nibler, J.W. Experiments in Physical Chemistry, 6th Edition, McGraw-Hill, New York, NY, 1996, pp 27-89.

2. Bettelheim, F. A., Experimental Physical Chemistry, W.B. Saunders Co., Philadelphia, 1971, Chapter 2.

3. Brownlee, K. A., Statistical Theory and Methodology in Science and Engineering, 2nd Edition, John Wiley and Sons, Inc., New York, New York, 1965, pp 334-338.

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14.1.7.9.12: Homework Problems

📅 **Pre-lab Due**: Attempt all seven problems before 1 pm on the scheduled meeting on this topic (see syllabus agenda). Your pre-lab assignment will be graded based on evidence of sincere effort, and work shown, but not on accuracy.

📅 **Final Problem Set Due**: The final problem set is due at 1 pm one week after our scheduled meeting on this topic (see syllabus agenda). The final problem set will graded based on work shown, thorough and accurate responses to questions, accuracy of calculation, and correct reporting (including units).

🎯 **Purpose:** Learn how to correctly estimate experimental uncertainty, and how to correctly report a value and its estimated uncertainty. This practice will get you ready to perform uncertainty analysis for your own experimental measurements this semester (and in the future).

Each practice problem below requires that you correctly apply either **statistical analysis** or **propagation of uncertainty** to estimate the uncertainty in a calculated value. Each problem also asks you to correctly report calculated values and their uncertainties.

Uncertainty analysis

This is the expected workflow for analysis of experimental values in P-Chem Lab:

Calculate → estimate uncertainty → report value ± uncertainty appropriately → justify the reporting → interpret what the uncertainty tells you.

Python (using Jupyter Notebooks in CoLab) is the recommended tool for completing this problem set. However, you may complete this assignment using any tool including pencil and paper, excel, etc. **You must understand the work you do, thus you may not use AI to complete this assignment.**

After submitting your initial attempts before the meeting, you will work with other students during our meeting to reach consensus about the strategies used to answer each question, and how to report each value and its uncertainty. Your instructors will be with you to answer your questions and to help guide your discussions. After the meeting, you will submit your revised work and final answers.

Your answers to these problems may be hand-written or typed. However, any submissions that are deemed illegible, unclear, or poorly organized will not be accepted.

Note

(1) We recommend that you use python to complete this problem set – we have provided some CoLab notebooks to help guide you. However, you may use whatever technology (calculators, software, etc.) you like to aid in working these problems.

(2) No matter what tools you use, it is important to show how your calculations are set-up and, where appropriate, give a sample calculation. Simply giving the final answer is not acceptable.

(3) In reporting all results, you should always round your reported answer to be consistent with your estimated uncertainty. For example: a calculated result of 56.2189 ± 0.0386 would be reported as **56.20 ± 0.04** where 0.04 is the standard deviation or propagated uncertainty. *See reading assignments for details about reporting*.

The seven problems are below. Note that there are custom CoLab tutorials to help you through this problem set. See Canvas and/or your Google Classroom to find the tutorials.

PROBLEM 1: Estimate Uncertainty using Statistics

A student makes five independent measurements of each of the linear dimensions of a box. The results are tabulated as follows:

Measurement	Length (cm)	Width (cm)	Height (cm)
1	1.010	5.376	2.001
2	1.015	5.339	2.105
3	1.013	5.385	1.985
4	0.999	5.375	1.989
5	1.009	5.369	2.008

A. **Summarize the measurements:** calculate the mean ($\bar{x}$), sample standard deviation (s), and relative standard deviation ($\%RSD = \frac{s}{\bar{x}} \times 100$). Report $\bar{x} \pm s$, and $\%RSD$ for each dimension (length, width, height) using appropriate units and appropriate precision.

B. **Compare the precision of the measurements**: Which dimension was most precise? ...least precise? Explain what statistical parameters from calculations in (A) are the most appropriate for comparing the precision of measurements that have different magnitudes. Support your answers using calculated values from (A).

C. **Calculate the volume**: Each row of the table represents one set of independent measurements of the box.
   - Calculate volume for each trial. This should produce five calculated volumes from the independent measurements of length, width, and height.
   - Then calculate the mean ($\bar{x}$), sample standard deviation (s), and relative standard deviation ($\%RSD$).
   - Report $\bar{x} \pm s$, and $\%RSD$ for volume using appropriate units and appropriate precision.

D. **Interpret results and justify choices for reporting:** Write a short paragraph that addresses the following points.
   - Which measurement (length, width, height) contributes the greatest uncertainty to the calculated volume?
   - Does the calculated volume appear to be more or less precise that the individual measurements? Explain, using evidence from your calcuations to support your argument.
   - Justify your choices in reporting to appropriate precision; in other words, what justifies "appropriate precision" of these values.

PROBLEM 2: A Simple Case for Propogation of Uncertainty

A student weighs a sample using an analytical balance, with an estimated uncertainty of ±0.5 mg in each measurement. Using the data below, determine the mass of the sample and the propagated uncertainty in that mass.

Item measured	Mass (g)
Sample and flask	5.1647 ± 0.0005
Empty flask (tare)	2.3712 ± 0.0005

A. Calculate the mass of the sample.
B. Calculate the propagated uncertainty in the sample mass.
C. Report the sample mass $\pm$ uncertainty: report using appropriate units and precision.
D. Explain why the propagated uncertainty is larger than the uncertainty in either individual mass measurement.
E. Justify the number of decimal places used in your final reported answer.

PROBLEM 3: Statistics and Rejection of Discordant Data

An investigator measures photon emission from the reaction shown below. The emitted photons (at 589 nm) are detected using a photomultiplier. For each run, the investigator measures both the total counts (signal + background) and the background counts.

$$Na^+ + O^- \rightarrow Na^* + O \overset{h\nu}{\rightarrow} Na + O$$

Run #	**Signal + Background (counts/sec)**	**Background (counts/sec)**
1	1500	1000
2	1200	1250
3	1375	1100
4	1425	900
5	1280	1200
6	1490	1363

The signal of interest is obtained by subtracting the background from the signal + background measurement.

A. **Determine the signal for each run.** Examine the resulting values before doing any further calculations. What do you notice about the data?
B. **Calculate the mean and standard deviation of the signal measurements.** Your software will probably display more digits than are meaningful. **Do not simply copy the numbers produced by the computer.** Decide how the mean and standard deviation should be reported, and explain your reasoning.
C. **One or more of these measurements might look suspicious.** Should any measurement be removed simply because it looks unusual? Explain briefly.
D. **Use the Q-test at the 90% confidence level to determine whether there is statistical justification for rejecting the suspicious measurement(s) as discordant.** Clearly identify the value(s) you test and compare Q_{calc} with Q_{crit}.
E. **Based on your statistical analysis, report your best estimate of the signal and its uncertainty.** Explain what the standard deviation tells you about the precision of this measurement, and is the standard deviation sufficient for estimating uncertainty? What other ideas might guide your decision for how to report the final value?

PROBLEM 4: Least Squares Analysis and Rejection of Discordant Data

The following experimental data are expected to show an approximately linear relationship between x and y.

Data Point	1	2	3	4	5	6	7
x	26	30	44	50	62	68	74
y	92	85	78	81	54	51	40

Your goal is to determine whether a linear model reasonably describes these data and to investigate whether there is statistical justification for rejecting any observation as an outlier.

A. **Plot and examine the data:** Create a scatterplot of y versus x. Before performing a regression, describe what you see.
   - Does a linear relationship appear reasonable?
   - Is the relationship positive or negative?
   - Does any point look unusual? If so, identify it.

B. **Fit a linear model:** Perform a linear least-squares regression and determine the slope, intercept, and correlation coefficient, r.
   - Add the best-fit line to your plot.
   - Report the equation of the fitted line on the plot, using an appropriate number of digits.
   - Report both the value and uncertainty for the slope and intercept. Justify your choices in reporting to appropriate precision; in other words, what justifies "appropriate precision" of these values.
   - Then interpret your result:
     - What does the **sign** of the correlation coefficient (r) tell you?
     - What does the **magnitude** of r tell you?
     - Does a large value of $|r|$, by itself, demonstrate that every observation is well described by the model? Explain.

C. **Examine the residuals:** For each observation, calculate the y-residual from the equation below (14.1.7.9.12.1) and create a plot of residual versus x.

$$\text{residual} = y_i - y_{predicted,i} \tag{14.1.7.9.12.1}$$

   - If the linear model adequately describes the data, what would you expect the residuals to look like?
   - Examine your residual plot. Do you see evidence of a systematic pattern, or does one observation appear particularly unusual? Identify the observation you would investigate further and explain your choice.

D. **Test the suspicious data point:** A point that looks unusual should not be discarded simply because removing it might improve the fit. Apply the **Q-test to the y-residuals** to determine whether there is statistical justification for rejecting the questionable observation. Compare Q_{expt} with the appropriate Q_{crit} at the **90% confidence level**. Based on this comparison, is there statistical justification for rejecting the observation? Explain your decision.

E. **What happens if the point is removed?** Regardless of your decision in Part D, temporarily remove the questionable observation and repeat the linear regression (Parts A, B, C above). This is an exploration, not permission to discard the measurement. Compare the regression **with and without** the suspicious data point. Consider slope, intercept, correlation coefficient r, and residuals.

F. **Make a scientific argument.** Did removing the questionable point substantially change the relationship between x and y? Support your conclusion with quantitative evidence from the two regression analyses.

PROBLEM 5: Propagation of Uncertainty

In a chemistry lab, students obtain the following data and are asked to find the **molecular weight (MW) of methanol** using the

ideal gas law, $PV = nRT$.

	Pressure (methanol)	Temperature	Mass (of methanol)	Volume
Trial 1	72.5 ± 0.5 mm Hg	295.10 ± 0.05 K	0.1331 ± 0.0002 g	1.05678 ± 0.00005 L
Trial 2	72.0 ± 0.5 mm Hg	295.05 ± 0.05 K	0.1329 ± 0.0002 g	1.05678 ± 0.00005 L

A. **Develop the function and determine MW**. Use the ideal gas law and the measured quantities to write a single expression for the molecular weight of methanol in grams per mole. Then calculate the molecular weight independently for each trial. ***Reminder**: pay attention to units, and perform unit conversions as necessary.*
B. **Propagate the uncertainty**. Determine the uncertainty in the molecular weight calculated for each trial. Clearly identify the uncertainty associated with each measured quantity and show how those uncertainties enter your calculation.
C. **Analyze the sources of uncertainty.** Which measured quantity contributes most strongly to the uncertainty in the calculated molecular weight? Support your answer quantitatively.
D. **Determine the average molecular weight and its uncertainty.** Calculate the average molecular weight determined from the two independent trials. Treat the two molecular wights as independently measured quantities and propagate their uncertainties through the calculation of the average. Report the average molecular weight and its uncertainty using appropriate units and precision.
E. **Justify your choices in reporting**. Explain how you determined the appropriate precision for the reported average molecular weight and its uncertainty.

PROBLEM 6: Propagation of Uncertainty

The Arrhenius relationship allows us to determine the activation energy for a reaction by measuring the rate constant at two different temperatures, according to the following expression.

$$ln\left(\frac{k_2}{k_1}\right) = -\frac{E_{act}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{14.1.7.9.12.2}$$

The rate constants for the reaction below was measured at two temperatures.

$$2DI \rightarrow D_2 + I_2$$

$k_{660} = (1.2 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $660 \pm 2K$

$k_{720} = (1.8 \pm 0.2) \times 10^{-3} \frac{liter}{mol\ sec}$ at $720 \pm 2K$

A. **Develop the function and determine the activation energy**. Use the Arrhenius expression (eq. 14.1.7.9.12.2) to develop a function for calculation of E_{act}. Then use the two independent measurements of k and T to calculate the E_{act}.
B. **Propagate the uncertainty in E_{act}.** Develop the function for calculation of uncertainty and determine the uncertainty in the value of E_{act}.
C. **Report and interpret the results.** Report E_{act} and its uncertainty using appropriate units and precision. Justify your choices in reporting.
D. **Analyze the sources of uncertainty.** Compare the contributions from k_1, k_2, T_1, and T_2. Which measurement(s) have the greatest influence on the uncertainty in E_{act}? Support your answer quantitatively.

PROBLEM 7: Propagation of Uncertainty

In the method of Clement and Desormes, the heat capacity (C) ratio of an ideal gas is determined from the manometrically determined values of P_1, the gas pressure at temperature T_1; P_2, the gas pressure immediately after a reversible adiabatic expansion when the temperature is T_2; and, P_3, the gas pressure after the gas has warmed back up to temperature T_1. The relationship used to calculate the heat capacity ratio is given by equation 14.1.7.9.12.3.

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{C_V}{R} + 1}{\frac{C_V}{R}} \tag{14.1.7.9.12.3}$$

where

$$\frac{C_V}{R} = \frac{P_2\left[1 - \left(\frac{P_3}{P_1}\right)\right]}{P_3 - P_2} \tag{14.1.7.9.12.4}$$

The following pressure data were collected:
P_1 = 763.1 ± 0.2 mmHg
P_2 = 757.0 ± 0.1 mmHg
P_3 = 758.7 ± 0.2 mmHg

A. **Develop the function and determine the heat capacity ratio, γ.** Use the equations above (eqs. 14.1.7.9.12.3 and \{refCD2}) to develop a function to calculate γ from the three pressure readings given above. Then use the function to calculate the value of γ.
B. **Propagate the uncertainty in each measured pressure to determine uncertainty in γ.** Calculate the uncertainty in the heat capacity ratio, γ.
C. **Report and interpret the result.** Report γ and its uncertainty with appropriate precision and units, if applicable. Justify your choices in reporting. Based on your uncertainty analysis, what can you conclude about the precision with which this experiment determines γ?

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14.1.7.10: ROTATION-VIBRATION SPECTRUM OF HCL AND DCL; VIBRATIONAL SPECTRUM OF SO2

Part I. The general approach to this experiment is adapted from Shoemaker, D.P., Garland, C.W. and Nibler, J.W., Experiments in Physical Chemistry, 6th edition, McGraw Hill Co. Inc, NY, 1996. In preparation for this experiment please read Experiment 37 in Shoemaker, Garland and Nibler beginning on page 397. You will want to read and understand the theory section including the subsections involving selection rules and isotope effects. In addition to this information the following section on transition intensities is offered.

Part II. The general approach to this experiment is adapted from D. P. Shoemaker, C. W. Garland, and J. W. Nibler, Experiments in Physical Chemistry, 6th edition, McGraw Hill Co. Inc, NY, 1996. In preparation for this experiment please read Experiment 35 in Shoemaker, Garland and Nibler beginning on page 383. You will want to read and understand the theory section including the subsections on the valence-force model and the vibrational partition function.

14.1.7.10.1: Data Analysis

14.1.7.10.2: Prelaboratory Exercise

14.1.7.10.3: Transition Intensities

14.1.7.10.4: Part I - FTIR spectrum of a mixture of HCl and DCl gas

14.1.7.10.5: Part II - FTIR spectrum of SO2

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14.1.7.10.1: Data Analysis

Data Analysis for HCl/DCl FTIR spectra

Note

This is one of the more laborious data analyses you will do this semester. Let's minimize the number of repetitive tasks to save you some time. The following shortcuts are recommended:

- **Collaborate with a partner on steps 1-3 (allowed in this specific case only)**:You may collaborate with your lab partners in steps 1-3 below. One student should work up the data (steps 1-3 ONLY) for $H^{35}Cl$ and $H^{37}Cl$, and the second student should do the same analysis for $D^{35}Cl$ and $D^{37}Cl$. You should then share your graphs of $\Delta\tilde{\nu}_{(m)}$ versus m and the values determined for the slopes and y-intercepts of these plots. Each student should do one complete analysis (either HCl or DCl) alone, and the other analysis can be the work of a partner. However, you are responsible for all work that is in your ELN, so be sure your partner's work is correct. *Steps 4 and onward should be completed individually, as usual.
- **Calculate errors for one isotope only**: The propagation of errors that you calculate for one isotope should similar (perhaps not identical, but close enough) as for another isotope. Save time by propagating errors carefully for (B_e, α_e, $\tilde{\nu}_o$, Ie, re, and k for one isotope, then use those errors as an approximation for the errors for analogous values for other isotopes.
- **Use what you know!** Do you remember that MatLab Introduction module way back in the beginning of this course? It was a long time ago, but it was a template for data analysis in this module! Go back and use what you already know, and what you already created as a template, for this data analysis.

Collaborate with a partner

1. Label each peak in your spectra as "P" or "R" and its J-value as: P(1), P(2),..., R(O), R(1),... etc., as shown in Figure 2 on page 399 of Shoemaker, Garland and Nibler. (**Note:** Spectra recorded using your iS50 FTIR spectrometer are plotted with the wavenumber (abscissa) decreasing from left to right.)
2. For each of the four isotopic combinations ($H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$), make a table of the m values and the corresponding peak frequencies $\tilde{\nu}_{(m)}$. For each isotopic combination, calculate the separation between adjacent peaks.

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} \tag{14.1.7.10.1.1}$$

Note

$\Delta\tilde{\nu}_{(m)}$ cannot be calculated for m = –1 since there is no peak for m = 0. Therefore m = –1 must be deleted from the vector of m values.

3. Plot the differences between adjacent absorption frequencies (i.e., $\Delta\tilde{\nu}_{(m)}$ versus m. Then perform a linear least squares fit of the data with the understanding that

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} = (2B_e - 3\alpha_e) - 2\alpha_e m \tag{14.1.7.10.1.2}$$

Use the standard deviations of the slope and intercept in your error analysis (Q14).

Work on your own

4. **Compute** B_e **and** α_e for each isotope from the intercept $(2B_e - 3\alpha_e)$ and the slope $-2\alpha_e$ of each best fit line (Equation 14.1.7.10.1.2).
5. **Calculate the frequency of the forbidden transition** $\tilde{\nu}_o$ using your calculated values of B_e and α_e. To do this, use equation 9 in expt 37 of Shoemaker, Garland and Nibler. The equation is $\tilde{\nu}_m = \tilde{\nu}_o + (2B_e - 2\alpha_e)m - \alpha_e m^2$. Calculate $\tilde{\nu}_o$ from several of the lines with low m values. Calculate the average value, and standard deviation, of $\tilde{\nu}_o$.

> **Note**
>
> You will get the best results by using only the lines closest to the center (e.g., m = ±1, ±2).

6. **Create a table** of $\tilde{\nu}_o$, B_e, and α_e for the four isotopic combinations The units should be cm^{-1}.
7. **Calculate the moment of inertia (I_e), and the internuclear distance (a.k.a. equilibrium bond length, r_e)** for all four isotopic combinations.
8. **Calculate the harmonic oscillator force constant, k,** for each isotopic combination from your calculated values of $\tilde{\nu}_o$. In doing so you will need to assume that $\tilde{\nu}_o$ and the harmonic oscillator frequency $\tilde{\nu}_e$ are the same, thus ignoring the effects of anharmonicity (see the formulas and discussion on pages 400 and 401 of Shoemaker, Garland and Nibbler).
9. **Compare your values of r_e and k with those reported in the literature.** Why are these values independent of isotopic substitution?
10. **Determine the isotope effects:** Compute the ratios $\frac{\tilde{\nu}_o^*}{\tilde{\nu}_o}$ and $\frac{B_e^*}{B_e}$ for ^{35}Cl and ^{37}Cl in the case of HCl, and again in the case of DCl. Compare these with the predicted values given by Eqs. (11) and (13) on page 400 of Shoemaker, Garland and Nibbler.
11. From the results in 10, above, **explain why is the ^{35}Cl /^{37}Cl isotope effect so much larger in DCl than it is in HCl?** That is, when looking at your FTIR spectrum, the ^{35}Cl/^{37}Cl line separation is significantly greater in the DCl case then when compared to the HCl case. A descriptive answer is a good start, but your experimental observations should also be supported with a calculation that justifies the experimental observation.
12. Apply the Boltzmann distribution to explain observed band intensities in terms of the populations of the ground-state levels (see the section on Transition Intensities in this manual). Again, a descriptive answer is a good start, but it should be supported with calculated results. You might create a spreadsheet to do these calculations. Does a calculation based on the Boltzmann population of rotational states match what you see experimentally in terms of which rotational lines show the greatest intensity?
13. From the mean line intensities for at least 10 features (for example five or more lines from the HCl spectrum and five or more from the DCl spectrum for a total of at least 10), determine the relative abundance of the two Cl isotopes. Estimate the weighted average atomic mass of Cl (that you might see on a periodic table for example) assuming that ^{35}Cl and ^{37}Cl have masses of 34.968 and 36.965 amu, respectively. Compare your result with the reported atomic mass of Cl.
14. For <u>one</u> isotope only, calculate the estimated uncertainty in each of the parameters determined for this experiment (B_e, α_e, $\tilde{\nu}_o$, I_e, r_e, and k). (Another table would be helpful)
15. Why is it important to purge the sample compartment of the FTIR spectrometer for both the background and sample runs? Why is it important to purge both background and sample for the same amount of time?

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14.1.7.10.2: Prelaboratory Exercise

Important note

Students in CHEM301L will only complete Part I of this module (HCl/DCl) and its related assignments.

Students in CHEM310L will complete all of this module, including both Part I (HCl/DCl) and part II (SO_2).

Reading assignment

This experiment involves many calculations; advanced knowledge of what you will have to do will be very helpful. In preparation for this experiment please read Experiment 37 in Shoemaker, Garland and Nibler beginning on page 397. You will want to read and understand the theory section including the subsections involving selection rules and isotope effects. In addition to this information read this module (not that there are two parts, and what you do depends on your course number). Additional references below are strongly recommended.

- Part I. Instrumentation, *Journal of Chemical Education,* **1986,** *63* (1), A5.
- Shoemaker, D.P., Garland, C.W., and Nibler, J.W. Experiments in Physical Chemistry, 6th ed., McGraw-Hill, New York, 1996, Chapter XIV, Experiments 35 and 37.
- McQuarrie, D.A. and Simon, J.D. "Physical Chemistry: A Molecular Approach", University Science Books, CA, 1997, Sections 13.2-13.4, 18.4-18.5); Atkins, P., Physical Chemistry, 5th ed., sections 16.8 – 16.11; and, Silbey, R.J., Alberty, R. A.
- Bawendi, M.G., Physical Chemistry, 4th ed., Sections 13.4, 13.6 and 13.7, for a discussion of rotation-vibration spectroscopy of diatomic molecules.

Written assignment

In addition to the usual prelab work expected for all experiments in the course (Introduction and Experimental Plan), please complete the following and submit the work prior to the lab meeting.

For Part 1 (CHEM310L and 301L), show which equations you would use to find: B_e; α_e; $\tilde{\nu}_o$; k; $\frac{\tilde{\nu}_o{}^*}{\tilde{\nu}_o}$; and $\frac{B_e^*}{B_e}$

For Part 2 (CHEM310L only), show which equations you would use to determine: k_1; $\frac{k_\delta}{\ell^2}$; $\tilde{C}_v(vib)$

Helpful videos

These videos provide a nice introduction and demonstration of the theory and techniques you will use.

Introduction to rotovibrational spectroscopy

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Filling a gas cell

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

14.1.2.2: Assignment Details

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14.1.7.10.3: Transition Intensities

Transition Intensities

The intensity of a spectral line depends not only on the transition probability and the frequency ν but also on the number of molecules in the initial state. Thus for a theoretical prediction of intensities, a knowledge of the numbers of molecules in the various initial states is necessary, in addition to a knowledge of the transition probabilities. Since most infrared (IR) spectra are observed under conditions of thermal equilibrium, we need only consider the distribution of the molecules over the different quantum states in thermal equilibrium.

According to the Boltzmann equation, the number of molecules dN_E that have a classical vibrational energy between E and $E + dE$ is proportional to $e^{-\frac{E}{k_B T}} dE$, where k_B is Boltzmann's constant and T is the absolute temperature. In quantum theory, only discrete values, $E_{(\nu)}$, are possible for the vibrational energy. The number of molecules in each of the vibrational states is then proportional to the Boltzmann factor $e^{-\frac{E_{(\nu)}}{k_b T}}$. The zero-point energy can be left out, since to add this to the exponent would only result in a multiplication factor that would be the same for all the vibrational levels (including the zero level).

The thermal distribution of the rotational levels (unlike that of the vibrational levels) is not simply given by the Boltzmann factor. We must account for the fact that, according to quantum theory, each state of an atomic system with total angular momentum J consists of 2J+1 energy levels which are degenerate in the absence of an external field; that is, the state has a (2J+1)-fold degeneracy. The number of molecules N_J in the rotational level J of the lowest vibrational state at the temperature T is thus proportional to

$$N_J \propto (2J+1)\, e^{-\frac{F_{(J)} hc}{k_B T}} \tag{14.1.7.10.3.1}$$

where $F_{(J)}$ is the rotational term value (equal to $\frac{E_{(J)}}{hc}$). For sufficiently large T or small rotational constant B, the population of the J^{th} rotational level, for N molecules, is given by the following equation [see p. 125 in reference (3)]

$$N_J = N \frac{hcB}{kT} (2J+1)\, e^{-\frac{B_J (J+1) hc}{kT}} \tag{14.1.7.10.3.2}$$

Since the factor 2J+1 increases linearly with J, the number of molecules in the different rotational levels goes through a maximum before decreasing with the rotational quantum number. It can be shown[3] that this maximum lies at

$$J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2} \tag{14.1.7.10.3.3}$$

This expression clearly shows that J_{max} increases with decreasing B and increasing T. It should be noted that the number of molecules in the lowest rotational level, J = 0, is not zero. With increasing temperature, the band extends over a wider frequency range and the intensity maxima of the two rotational branches move outward and at the same time become flatter.

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14.1.7.10.4: Part I - FTIR spectrum of a mixture of HCl and DCl gas

Note

The ELN for this entire experiment is here: ELN03_FTIR2022.docx

In preparation for this experiment, read your textbook (McQuarrie, D.A. and Simon, J.D. "Physical Chemistry: A Molecular Approach", University Science Books, CA, 1997, Sections 13.2-13.4, 18.4-18.5); Atkins, P., Physical Chemistry, 5th ed., sections 16.8 – 16.11; and, Silbey, R.J., Alberty, R. A. and Bawendi, M.G., Physical Chemistry, 4th ed., Sections 13.4, 13.6 and 13.7, for a discussion of rotation-vibration spectroscopy of diatomic molecules. Each pair of students may share some of the data analysis as described in Section 4.3.3.

Preparation of Gas Sample Cell

- A mixture of HCl and DCl will be introduced into an IR gas cell. Note that because natural chlorine is a mixture of two isotopes ^{35}Cl and ^{37}Cl (in a ratio of 3 to 1), this sample is a mixture of four different gases, each with a distinct spectrum.
- Hydrogen chloride and deuterium chloride are **colorless, pungent, and corrosive gases** that fume in air. Contact will cause **burns to the skin, severe burns to the eyes and burns to the respiratory system if inhaled.** A vacuum line will be used to transfer the gases from their high-pressure containers to an evacuated IR cell.
- When not in use the IR gas cell must be stored in the desiccator. The cell is constructed of a glass body with KBr windows at each end. Ensure that the salt windows are kept free of moisture at all times. Please do not touch these windows.

Vacuum-Line Start-Up

Most of the following will be completed by the TA before the lab period.

1. Check that all external valves on the working and main manifold are closed to the outside atmosphere.
2. Attach an empty N_2 trap to the main manifold. *Hold this trap in place until a vacuum has formed.*
3. Turn on the floor vacuum pump to start generating a vacuum.
4. Turn on all valves in the manifold that are connected to gages (marked with purple tape).
5. Turn on the diffusion pump.
    - Ensure that the floor pump is on BEFORE the diffusion pump. Otherwise, the diffusion pump will generate heat and the oil within the pump will oxidize, causing long-term damage to the diffusion pump.
6. Turn on Digivac electronic monitor. Use this to actively monitor the pressure at the end of the main manifold.
7. Check the analog pressure gauge on the diffusion pump to ensure the pressure is stable.
    - Throughout the experiment, the pressure should remain below 30 mtorr if the system is closed and stable.
8. Fill a 4L dewar with liquid N_2 from the shared Chemistry department supply.
9. Place a second dewar underneath the N_2 trap and fill with liquid N_2 from the 4L dewar such that the N_2 trap is submerged in liquid N_2
10. Check the level of N_2 as the experiment progresses. Refill if necessary to ensure the trap remains cold.
11. Check to ensure the pressure at the end of the main manifold is below 30 mtorr before proceeding.

Transferring HCl and DCl to gas cell

1. Remove gas cell from the desiccator and attach to the middlemost section of the working manifold shown below in Figure 14.1.7.10.4.1.

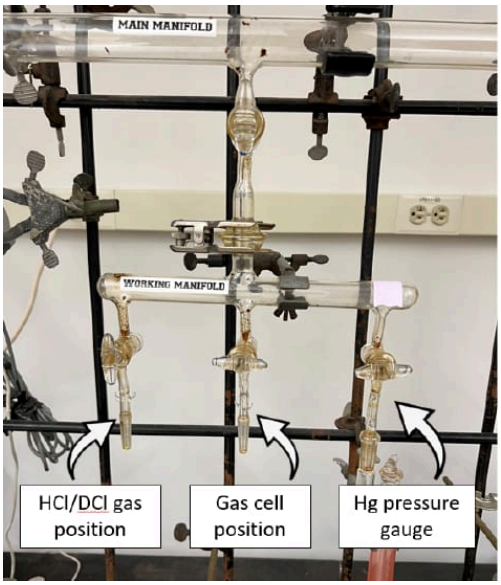


Figure 14.1.7.10.4.1: Vacuum line set-up: working manifold and main manifold

2. Evacuate the back of the gas cell and introduce a vacuum to the interior of the cell.
3. Remove cell from manifold, bring it to the FTIR instrument, and take a background spectrum (see "Obtaining an FTIR Spectrum using the Nicolet iS50" below).
4. Replace the gas cell onto the working manifold and open it to vacuum.
5. Connect the pressurized HCl cannister to the working manifold via a vacuum-rated line. This line should contain its own needle valve that may be closed to separate the cannister from the rest of the working manifold. Introduce a vacuum to the line and to the pocket between this needle valve and the main valve on the cannister. The HCl cannister should remain closed at this time. Close the needle valve once this pocket has been evacuated.
6. Close the working manifold off from the main manifold.
7. Introduce a small amount of HCl gas to the pocket between the cannister and the needle valve by turning the cannister's main valve 180 degrees open briefly, and returning 180 degrees to close the cannister once more.
8. After ensuring the HCl cannister is closed, open the needle valve to release HCl into the working manifold. Use the mercury pressure gauge on the working manifold to monitor this process.
    - If the pressure rises such that it threatens to expel mercury from the pressure gauge, open the working manifold to the main manifold to release pressure.
9. Slowly release HCl from the working manifold using the valve to the main manifold until the pressure in the gas cell reaches 10 mmHg.
10. Close the gas cell off from the working manifold and open the working manifold to the main line to release any excess HCl from the rest of the system. (Remember to include the pocket between the needle valve and the HCl cannister!)
11. Repeat steps 5-10 using DCl gas to introduce an additional 10 mmHg DCl into the gas cell such that the final contents of the cell are 10 mmHg HCl and 10 mmHg DCl. (What pressure DCl needs to be introduced to the working manifold for this to happen? *Hint: it's not 10 mmHg.*)
12. Record HCl/DCl spectrum using "Obtaining an FTIR Spectrum using the Nicolet iS50" below.
13. Once all data has been collected, return the gas cell to the working manifold and safely evacuate all remaining HCl/DCl.
14. Close and remove the evacuated gas cell and return it to the desiccator.

Vacuum Line Shutdown

1. Turn off the diffusion pump. Wait 5 mins for the pump to cool.
    - The pump should be cool before any oxygen is introduced to the system to prevent oil in the pump from oxidizing.
2. Close all valves with purple tape.
3. Turn off Digivac monitor.
4. Turn off the floor pump.
5. Pick an external valve and open it to release the vacuum and open both the working manifold and the main manifold to the air.
    - Do this quickly after step 4. The system should not be left under vacuum without an active vacuum pump.

6. Remove N_2 trap and transfer it to the fume hood to safely evaporate excess HCl/DCl gas.
    1. Do this quickly after step 5. Leaving the N_2 trap cold after the vacuum has been released may cause liquid O_2 to condense, which is highly volatile.

Obtaining an FTIR Spectrum using the Nicolet iS50

You will use a Nicolet iS50 FT-IR Fourier Transform Infrared (FTIR) Spectrometer to collect FTIR spectra. Below are instructions for its use.

1. Check the sample holder in the spectrometer to make sure there is nothing blocking the path of the infrared beam. Close the cover of the instrument.
2. The Omnic software may already be loaded. If not, load it by clicking the 

icon on the Windows desktop. As the software loads you will a blue light appear on the right side of the instrument and the main window with the menu items and button bar.



Figure 14.1.7.10.4.1: The Omnic Button Bar. (CC-NC-BY-DUKE CHEM)

Note on Collecting Data

This is a single beam instrument. You must first record a background interferogram of the evacuated gas cell. A fast Fourier transform (FFT) will then be performed to give background transmittance spectrum. You will then introduce your gas sample into the SAME gas cell and record a new interferogram. FFT analysis of this interferogram will give a single beam *transmittance* spectrum of your sample. This spectrum is then ratioed against the single beam background spectrum to give the transmittance spectrum of your sample. Finally the absorbance spectrum of your sample is calculated and displayed.

3. Open the sample compartment of the FTIR spectrometer and mount the evacuated gas cell on the gas cell holder. Close the cover and allow the sample compartment to be purged with dry, CO_2-free air for at 5 minutes, noting the time so that the purge time is reasonably accurate.
4. Check the **Experiment Setup** from the **Collect** menu. It should be set to run 8 scans at 0.125 Cm^{-1} resolution. You should be working in Absorbance format and a background scan should be "good" for 200 minutes.

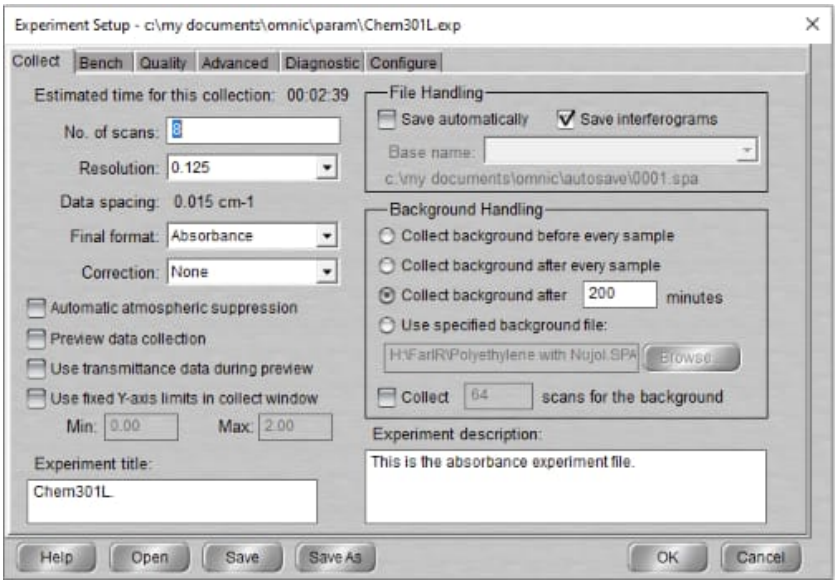


Figure 14.1.7.10.4.2: The Collect Pane of the Experiment Setup Window. (CC-NC-BY-DUKE CHEM)

Click on the **Bench** tab and wait for the interferogram to appear. The **Max** signal should be around 4.5. Click **OK**.

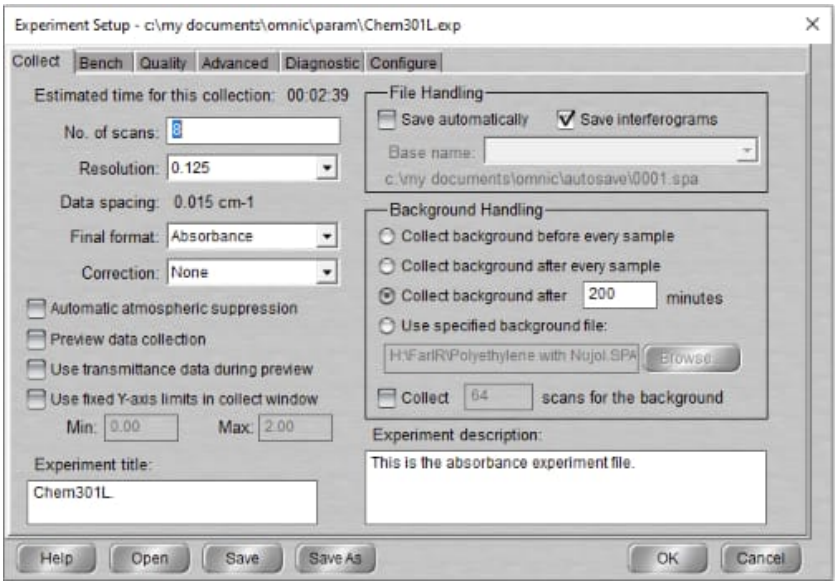


Figure 14.1.7.10.4.3: The Bench Pane of the Experiment Setup Window. (CC-NC-BY-DUKE CHEM)

5. Select **Collect Background** from the **Collect** menu (or with the **Col Bkg** button). Click **OK** when you see the **Confirmation** box. It will take about 4 minutes for the background scan to complete. Part way through, the background scan will be displayed on the main software screen. Once complete, add the spectrum to the window when prompted. Note the presence of water vapor and CO_2 in the spectrum. This arises from the atmosphere surrounding the cell (Remember: you gas cell is evacuated at this point). Keep a copy of the background both as a file (**File** → **Save as**), and take a screen shot for your ELN.

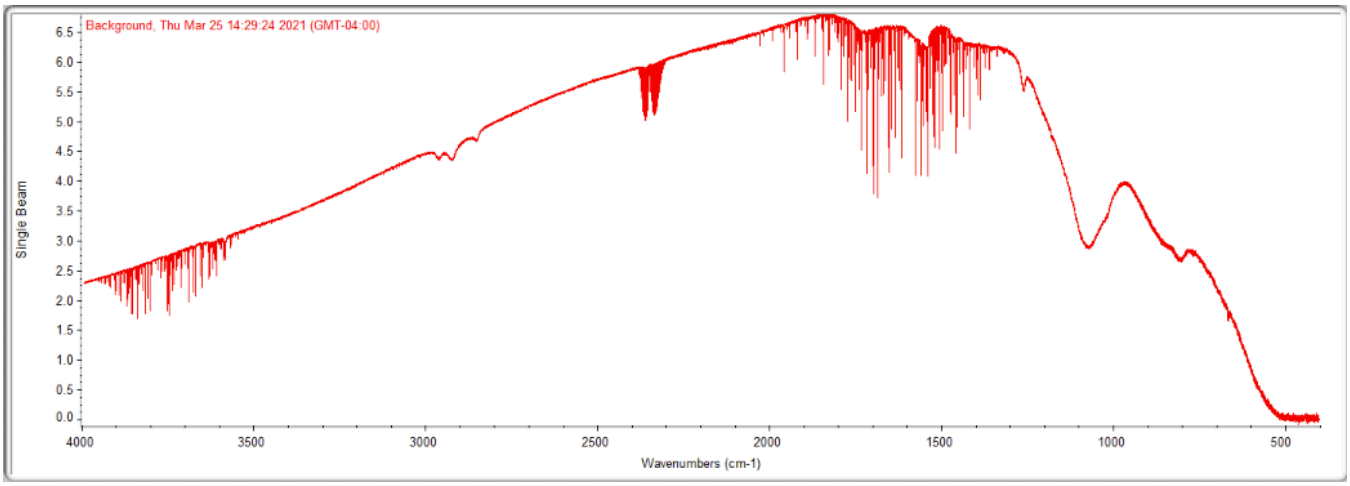


Figure 14.1.7.10.4.4: A Typical Background Spectrum. (CC-NC-BY-DUKE CHEM)

6. Remove the evacuated gas cell from the sample compartment. Under the guidance of your TA, introduce first 1 cm Hg pressure of DCl gas followed by about 0.8 cm Hg pressure of HCl gas into the cell. You must be careful to avoid the introduction of air into the cell. Replace the gas cell on the sample holder, and close the door of the sample compartment. Allow the sample compartment to purge for the same time as in the background spectrum.
7. Select **Collect Sample** from the **Collect** menu (or use the **Col Smp** button). You can enter a title or leave the default date/time when prompted. Click **OK**, and **OK** again in the Confirmation box to start the run.
8. When the scan is complete, add the scan to the window and you will see both sample and background displayed. **Save** the data file (**F**ile → **Save as**).

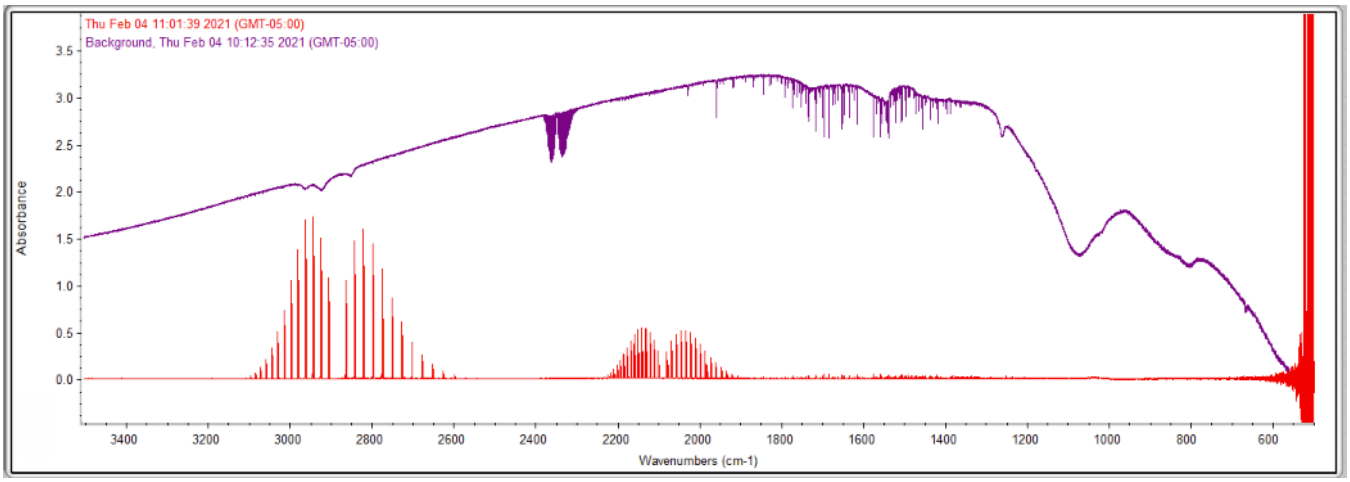


Figure 14.1.7.10.4.5: Sample and Background Together. (CC-NC-BY-DUKE CHEM)

Click on the background scan and select **Hide Spectra** from the **View** menu to remove the background spectrum from view.

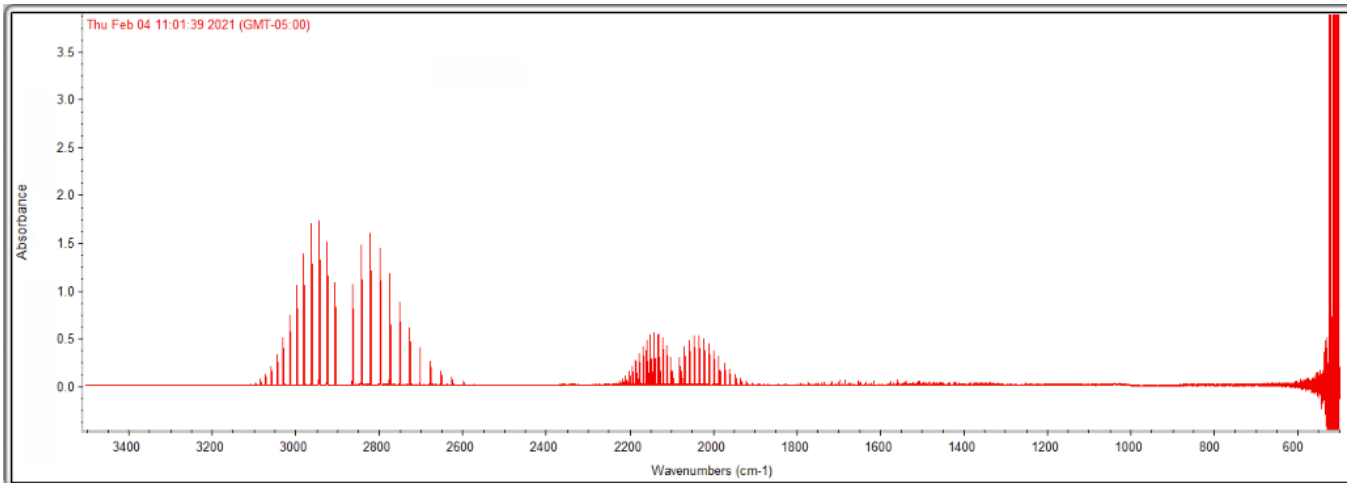


Figure 14.1.7.10.4.6: The Sample Spectrum. (CC-NC-BY-DUKE CHEM)

9. You will see two (or three) sets of peaks in the region 3200-1800 cm–1. Which of these is the spectrum of HCl and which the spectrum of DCl? Explain your reasoning. In your report, explain the origin of the third set of peaks (if observed). Click and drag a box around the $H^{35}Cl/H^{37}Cl$ absorption and double-click in the box to expand the scale so that the spectrum of fills the screen.

10. Select **Find Peaks** from the **Analyze** menu or click the 

button. Move the horizontal threshold bar down so that it captures as many of the peaks as possible without getting into the noise at the baseline (see Figure 4.3.7 below). You can also adjust the **sensitivity** slider at the left of the screen to fine tune the peak selection. When you have a good selection of peaks, click the **Clipboard** button to put the peaks table into the Windows Clipboard. Open Excel and paste the clipboard into a spreadsheet. Save the spreadsheet along with a screenshot of the peak positions overlaid onto the speactum as seen in Figure 4.3.7.

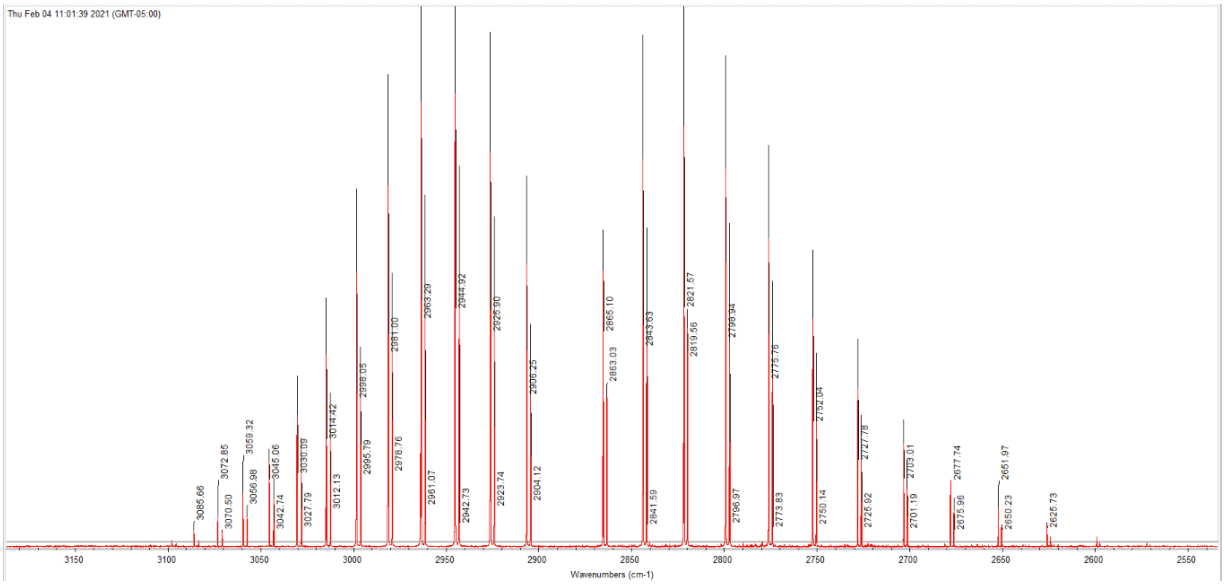


Figure 14.1.7.10.4.7: the Find Peaks Function. (CC-NC-BY-DUKE CHEM)

11. Click Replace at the top right of the screen to bring you back to the active window. Click and drag the white selection window over to the DCl spectrum.

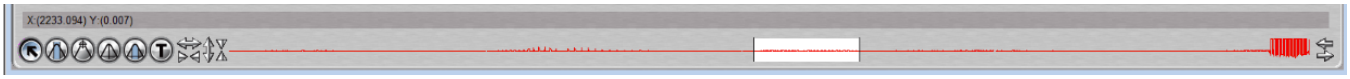


Figure 14.1.7.10.4.8: The Selection Window. (CC-NC-BY-DUKE CHEM)

Re-scale the DCl spectrum in the window and repeat the peak-finding steps being sure to add the resultant peaks table to your Excel spreadsheet.

12. Save screen shots of the spectra and the report for your ELN.
13. If you wish to record the spectrum of a new sample, say of SO_2 in Part 2 of this experiment, repeat steps (4.3.2.6)-(4.3.2.12).
14. When you are done with the instrument and all of your work is saved, close the software. You will notice the blue light on the instrument turn off as the instrument goes into standby mode.
15. Remove your sample from the sample compartment and **close the cover**.
16. Re-evacuate the gas cell to remove your sample and store the evacuated cell (with stopcocks closed) in the desiccator.

Data Analysis for HCl/DCl FTIR spectra

Note

This is probably the most intense data analyses you will conduct this semester. Let's minimize the number of repetitive tasks to save you some time. The following shortcuts are recommended:

- **Collaborate with a partner on steps 1-3 (allowed in this specific case only)**:You may collaborate with your lab partners in steps 1-3 below. One student should work up the data (steps 1-3 ONLY) for $H^{35}Cl$ and $H^{37}Cl$, and the second student should do the same analysis for $D^{35}Cl$ and $D^{37}Cl$. You should then share your graphs of $\Delta\tilde{\nu}_{(m)}$ versus m and the values determined for the slopes and y-intercepts of these plots. Each student should do one complete analysis (either HCl or DCl) alone, and the other analysis can be the work of a partner. However, you are responsible for all work that is in your ELN, so be sure your partner's work is correct. *Steps 4 and onward should be completed individually, as usual.
- **Calculate errors for one isotope only**: The propagation of errors that you calculate for one isotope should similar (perhaps not identical, but close enough) as for another isotope. Save time by propagating errors carefully for (B_e, α_e, $\tilde{\nu}_o$, Ie, re, and k for one isotope, then use those errors as an approximation for the errors for analogous values for other isotopes.
- **Use what you know!** Do you remember that MatLab Introduction module way back in the beginning of this course? It was a long time ago, but it was a template for data analysis in this module! Go back and use what you already know, and what you already created as a template, for this data analysis.

Collaborate with a partner

1. Label each peak in your spectra as "P" or "R" and its J-value as: P(1), P(2),..., R(0), R(1),... etc., as shown in Figure 2 on page 399 of Shoemaker, Garland and Nibler. (**Note:** Spectra recorded using your iS50 FTIR spectrometer are plotted with the wavenumber (abscissa) decreasing from left to right.)
2. For each of the four isotopic combinations ($H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$), make a table of the m values and the corresponding peak frequencies $\tilde{\nu}_{(m)}$. For each isotopic combination, calculate the separation between adjacent peaks.

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} \tag{14.1.7.10.4.1}$$

Note

$\Delta\tilde{\nu}_{(m)}$ cannot be calculated for m = –1 since there is no peak for m = 0. Therefore m = –1 must be deleted from the vector of m values.

3. Plot the differences between adjacent absorption frequencies (i.e., $\Delta\tilde{\nu}_{(m)}$ versus m. Then perform a linear least squares fit of the data with the understanding that

$$\Delta\tilde{\nu}_{(m)} = \tilde{\nu}_{(m+1)} - \tilde{\nu}_{(m)} = (2B_e - 3\alpha_e) - 2\alpha_e m \tag{14.1.7.10.4.2}$$

Use the standard deviations of the slope and intercept in your error analysis (Q14).

Work on your own

4. **Compute** B_e **and** α_e for each isotope from the intercept $(2B_e - 3\alpha_e)$ and the slope $-2\alpha_e$ of each best fit line (Equation 14.1.7.10.4.2).
5. **Calculate the frequency of the forbidden transition** $\tilde{\nu}_o$ using your calculated values of B_e and α_e. To do this, use equation

9 in expt 37 of Shoemaker, Garland and Nibler. The equation is $\tilde{\nu}_m = \tilde{\nu}_o + (2B_e - 2\alpha_e)m - \alpha_e m^2$. Calculate $\tilde{\nu}_o$ from several of the lines with low m values. Calculate the average value, and standard deviation, of $\tilde{\nu}_o$.

> **Note**
>
> You will get the best results by using only the lines closest to the center (e.g., m = ±1, ±2).

6. **Create a table** of $\tilde{\nu}_o$, B_e, and α_e for the four isotopic combinations The units should be cm^{-1}.
7. **Calculate the moment of inertia (I_e), and the internuclear distance (a.k.a. equilibrium bond length, r_e)** for all four isotopic combinations.
8. **Calculate the harmonic oscillator force constant,** k, for each isotopic combination from your calculated values of $\tilde{\nu}_o$. In doing so you will need to assume that $\tilde{\nu}_o$ and the harmonic oscillator frequency $\tilde{\nu}_e$ are the same, thus ignoring the effects of anharmonicity (see the formulas and discussion on pages 400 and 401 of Shoemaker, Garland and Nibbler).
9. **Compare your values of r_e and k with those reported in the literature.** Why are these values independent of isotopic substitution?
10. **Determine the isotope effects:** Compute the ratios $\frac{\tilde{\nu}_o^*}{\tilde{\nu}_o}$ and $\frac{B_e^*}{B_e}$ for ^{35}Cl and ^{37}Cl in the case of HCl, and again in the case of DCl. Compare these with the predicted values given by Eqs. (11) and (13) on page 400 of Shoemaker, Garland and Nibbler.
11. From the results in 10, above, **explain why is the ^{35}Cl /^{37}Cl isotope effect so much larger in DCl than it is in HCl?** That is, when looking at your FTIR spectrum, the ^{35}Cl/^{37}Cl line separation is significantly greater in the DCl case then when compared to the HCl case. A descriptive answer is a good start, but your experimental observations should also be supported with a calculation that justifies the experimental observation.
12. Apply the Boltzmann distribution to explain observed band intensities in terms of the populations of the ground-state levels (see section 4.2). Again, a descriptive answer is a good start, but it should be supported with calculated results. You might create a spreadsheet to do these calculations. Does a calculation based on the Boltzmann population of rotational states match what you see experimentally in terms of which rotational lines show the greatest intensity?
13. From the mean line intensities for at least 10 features (for example five or more lines from the HCl spectrum and five or more from the DCl spectrum for a total of at least 10), determine the relative abundance of the two Cl isotopes. Estimate the weighted average atomic mass of Cl (that you might see on a periodic table for example) assuming that ^{35}Cl and ^{37}Cl have masses of 34.968 and 36.956 amu, respectively. Compare your result with the reported atomic mass of Cl.
14. For one isotope only, calculate the estimated uncertainty in each of the parameters determined for this experiment (B_e, α_e, $\tilde{\nu}_o$, I_e, r_e, and k). (Another table would be helpful)
15. Why is it important to purge the sample compartment of the FTIR spectrometer for both the background and sample runs? Why is it important to purge both background and sample for the same amount of time?

References and further Reading for Part I

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14.1.7.10.5: Part II - FTIR spectrum of SO2

Reminder

The general approach to Part II of this experiment is adapted from D. P. Shoemaker, C. W. Garland, and J. W. Nibler, Experiments in Physical Chemistry, 6th edition, McGraw Hill Co. Inc, NY, 1996. In preparation for this experiment please read Experiment 35 in Shoemaker, Garland and Nibler beginning on page 383. You will want to read and understand the theory section including the subsections on the valence-force model and the vibrational partition function.

Prepare the sample of SO_2

A vacuum line will be used to evacuate the IR gas cell of HCl/DCl gas. Then transfer the toxic SO_2 gas from its high-pressure containers to the evacuated IR cell. The cell should be loaded with SO_2 to a pressure of $0.5 - 1.0$ cm Hg. Use assistance from your TA and use the protocols and precautions described earlier as a guide.

Note

You will use a pressure of SO_2 less than or equal to 1 cm Hg. If the pressure of SO_2 in the gas cell is much higher, you will not be able to observe the fine structure on the most intense fundamental frequency. If the gas pressure is too low, you may not be able to observe the weak combination bands. Depending on your skill with transferring known pressures of gases on the vacuum line, you may find it easier to record the spectrum using two different gas pressures so that all the features of the spectrum are well resolved.

Collect the FTIR spectrum of SO_2

Use the protocols and precautions described earlier as a guide.

1. Record an FTIR absorbance spectrum of SO_2 at 0.125 cm^{-1} resolution, and under the same conditions used for the HCl/DCl sample, and ratio against the background spectrum of the evacuated cell.
2. Plot the absorbance spectrum over the range $4000 - 400\ \ cm^{-1}$ (or a range suggested by your TA). Determine the frequency of each band seen in the spectrum. Inspect the data carefully and identify combination bands and overtone bands that are visible in the spectrum.
3. Use the Omnic **Annotation Tool** (look to the bottom of the spectrum window for the  button) to label the center position of each fundamental band and of any overtone or combination bands you observe.
    - You use this tool by clicking on the  button, position the cursor (now with an associated T) at the point you want to measure.
    - Then click and drag a line up (maybe up and over).
    - When you click again the wavelength at that position on the spectrum will be added as an annotation to the spectrum (see picture).
    - If you want to delete an annotation, drag a box around the annotation (the actual wavelength added to the screen) and select **Delete Annotation** from the **Edit** menu.

Note

Notice that in determining the frequency of vibration in you are estimating the center of the feature by eye and hand, rather than having the Omnic software determine the peak position. To get an estimate of the uncertainty of your determination, do between three and five repeated trials of estimating the frequency and find the mean and standard deviation.

Notice also that because we are using both an instrument and a gas cell with KBr windows, we will not be able to see the bending mode clearly or completely as the KBr starts to absorb strongly in that region of the spectrum. You should, however, see enough of the bending mode to get a crude estimate of its frequency. Get help from your TA, and comment in your ELN why this frequency may show greater deviation from expected values than the others.

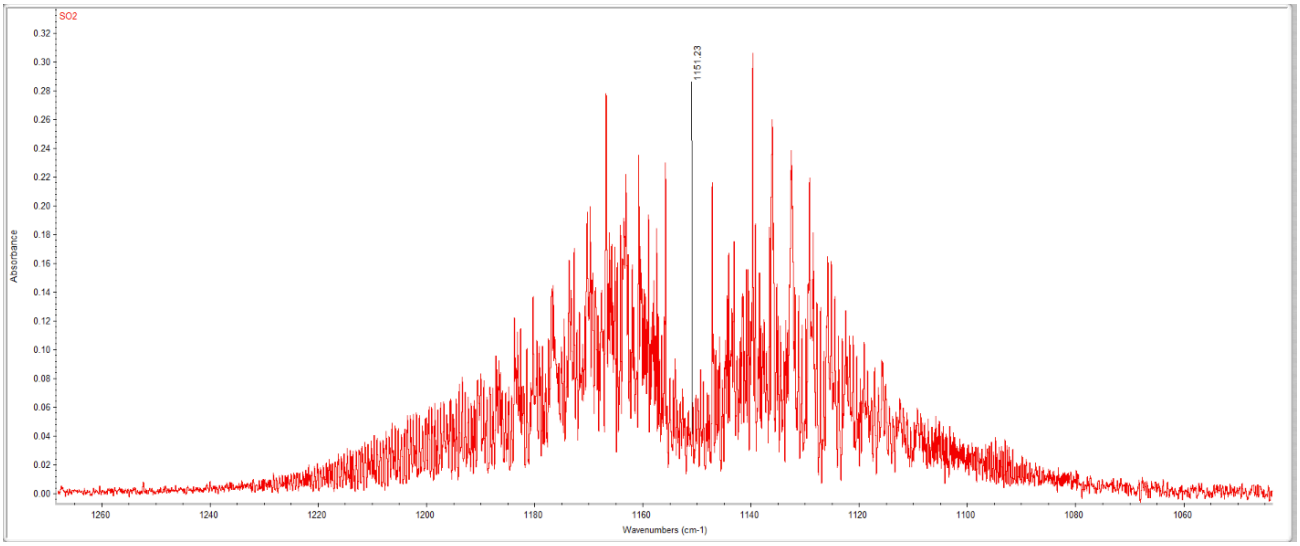


Figure 14.1.7.10.5.1: The Symmetric Stretch of $SO_{2(g)}$. (CC-NC-BY-DUKE CHEM)

Clean up/ Shut down

Please use the vacuum line to evacuate the gas cell and store the evacuated cell in the desiccator. Please work under supervision of your instructor to shut down the gas line using the protocols and precautions described earlier as a guide.

Treatment and Analysis of Data

1. Assign the fundamental bands of SO_2 as: symmetric stretch, $\tilde{\nu}_1$; bend, $\tilde{\nu}_2$; asymmetric stretch, $\tilde{\nu}_3$; and, report their frequencies. Compare your value with those reported in the literature.
2. Then assign any other bands, comparing the observed frequencies with those calculated from combinations of the fundamental values $\tilde{\nu}_1$, $\tilde{\nu}_2$, $\tilde{\nu}_3$.
3. Calculate k_1 and $\frac{k_\delta}{\ell^2}$ from Equations (1) and (3) (on page 385 of Shoemaker, Garland and Nibler) using your values of $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_3$. Check the valence-force model by calculating both sides of Eq. (2) (also on p. 385 of Shoemaker) and comparing them. Again, compare your results with literature values.

Note

When finding literature values for the force constants of SO_2, you will likely notice that different notations are used. It may be difficult to find the k_1 and $\frac{k_\delta}{\ell^2}$ notation used in Shoemaker, Garland and Nibler (and as such in this manual). For example, Kivelson[8] reports these same vales as f_d; and, $\frac{f_a}{d^2}$ and reports the values in units of $\frac{dynes}{cm}$ rather than $\frac{N}{m}$. Be prepared to convert.

4. Using your values of $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_1$, calculate $\tilde{C}_{v(vib)}$ at 298 K and at 500 K from Eq. (8) on page 386 of Shoemaker, Garland and Nibler.
5. At these same temperatures, calculate $\tilde{C}_v$ from the expression

$$\tilde{C}_v = 3R + \tilde{C}_{v(vib)} \tag{14.1.7.10.5.1}$$

and compare your results with the following $\tilde{C}_v$ values (obtained from directly measured values of $\tilde{C}_p$ and the expression

$$\tilde{C}_v = \tilde{C}_p - R \tag{14.1.7.10.5.2}$$

$\tilde{C}_v$ = 30.5 J K^{-1} mol^{-1} at 298 K and 37.7 J K^{-1} mol^{-1} at 500 K.
6. Calculate the uncertainty of each result you report in this experiment.

References and further reading

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15.5.3: Invoking Matlab From the Lab Computers

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15.1: Pre-lab Assignment

📅 **Due:** This assignment must be completed before 1:00 PM on your first lab meeting day (see syllabus schedule).

🕒 **Time:** Plan at least two hours to complete this assignment. If you run into technical challenges, this will take additional time.

🎯 **Purpose**: This pre-meeting assignment is designed to help you arrive to our first meeting prepared to complete course-specific MatLab training.

Pre-Lab assignment for MatLab

To prepare for the laboratory session on MatLab, please do the following prior to the laboratory period:

- Download and install MatLab on your personal laptop computer (see get access section).*
  - During MatLab Installation, select all of the following additional "Toolboxes":
    - Statistics and Machine Learning Toolbox
    - Curve Fitting Toolbox
    - Symbolic Math Toolbox
- Download the custom scripts and binary files (Get Scripts Here), and put these files in the default MatLab directory on your computer.
- Learn the basics: Proceed through the first two Matlab Getting Started tutorials that are provided when you open the software (Desktop Basics and Matrices and Arrays).
- Complete the Pre-Lab quiz on Canvas.
- Bring your computer, with MatLab installed, to the lab meeting.
- This ession is a "Dry Lab": We will meet in a classroom, thus lab attire is not necessary for this session.

*It is recommended that you install MatLab on your own computer, but there are other way to access MatLab if necessary (get access).

Be sure you complete the assignment above, including the online quiz on Canvas, before the deadline!

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15.2: MATLAB PRACTICE (IN CLASS ACTIVITY)

Note

Before attempting these exercises, please make sure you have access to a working copy of the MatLab software and you have the custom scripts and binary files installed in the MatLab directory. If you are using FastX to access MatLab on campus, these files are already installed for you on the server. Otherwise, you should install MatLab and the custom files on your computer before proceeding.

The practice exercises in this module are meant to be completed during the scheduled meeting. The Matlab practice exercises are are designed to help you become literate in MatLab programing language and the MatLab GUI's so that you can accomplish the data analysis in this course. MatLab is the preferred tool for data analysis for the modules later in this lab semester.

Both of the activities below can be completed during the first laboratory meeting; collaboration among students is welcome, though each of you should complete the activity and submit your own work. Your work should be inspected by your teaching assistant (TA) before you submit the assignments and leave for the day. If your TA determines that you have done the activities correctly, you will receive full credit for this assignment.

15.2.1: The Basics

15.2.2: Practice with LiveScript

15.2.3: MatLab for Data Analysis In This Course

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15.2.1: The Basics

Originally Created by Lindsay Pederson, Fall 2022 | Modified by Kathryn Haas each semester since.

Caution

This exercise may be an uncomfortable experience if you haven't completed the basic MATLAB tutorials that were part of your pre-lab assignment. If you are feeling lost during this activity, please go back to the basic MATLAB tutorials to get comfortable with the basic commands and practice working with matrices before returing to this exercise.

MatLab General Layout

Open the MatLab program to begin. If the layout of your MatLab window looks different than the arrangement illustrated below, you can switch to the default layout using the "Layout" button in the Home Tab toolbar (see below). Choose "Default Layout" from the "Layout" drop down menu. If the layout still seems different than what is shown it might be because you have a Script or LiveScript file open in your MatLab program.

Compare your MatLab window to what is shown below. Read the figure below and familiarize yourself with the panels of the MatLab window. Then follow the instructions.

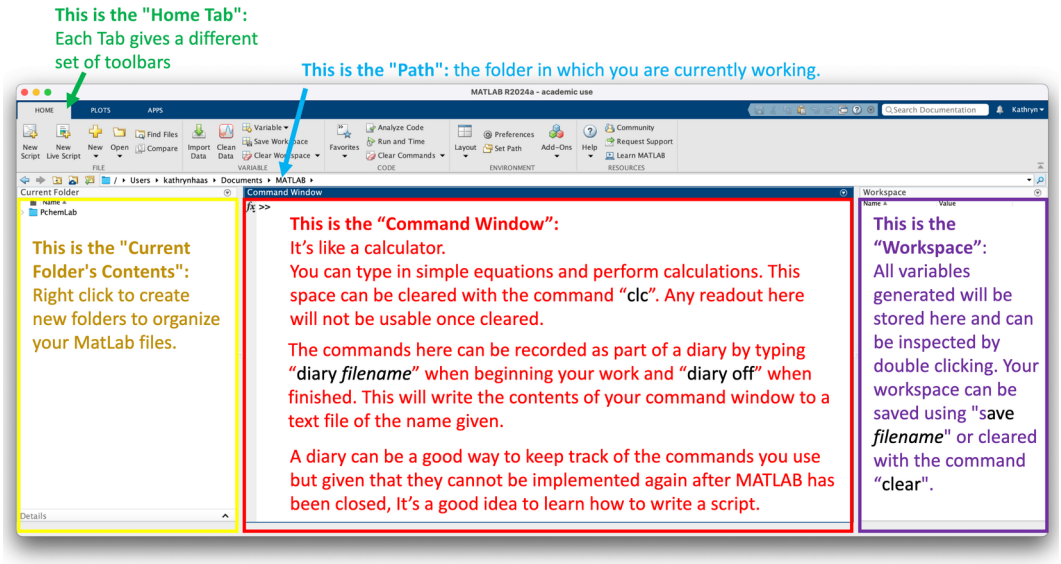


Figure 15.2.1.1: The default layout of the MatLab window (as of version R2024a). The tabs above the top toolar give access to different toolbar options. The file path is shown under the top toolar and indicates the current working folder. The Current folder's contents is shown in the pannel on the left. The center window is the Command Window, which functions like a calcuator. Type commands into the command window, save the work in the command window using the "diary filename" command to start saving and "diary off" when finished. All variables enterend in the Command Window will be populated in the Workspace, shown in the panel on the right. The Workspace can be saved using the "save filename" command or by using the "save workspace" button in the Home Tab toolbar. The workspace can be cleared using the "clear" command. (CC-NC-BY-SA; Kathryn Haas)

Practice with the Command Window

Find the command window in MATLAB. The command window is like a calculator. You can type simple equations here to perform calculations. The command window can be cleared by the command:

```
clc
```

All work is lost after the space is cleared.

The commands entered in the command window can be recorded in a text file (a diary). To record a diary, use the command "diary filename" at the beginning of your work:

```
diary filename
```

And then then at the end of the work:

```
diary off
```

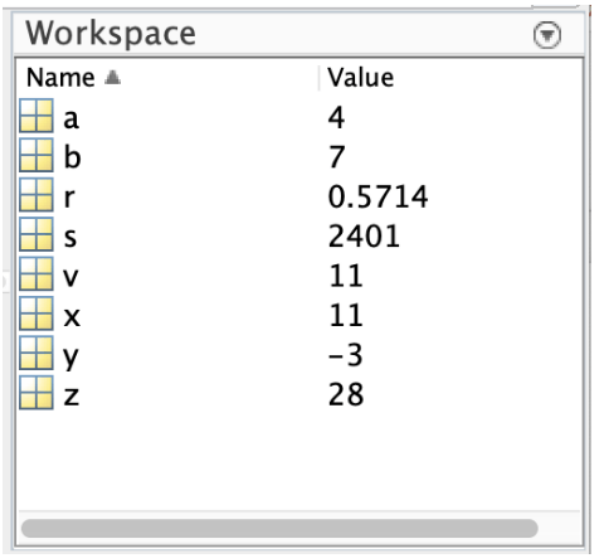
The diary file is a good way to keep track of commands, but the work cannot be implemented again from the diary file, so it has limited utility. **Script** and **Live Script** files are a much more useful way to record your work. **First, let's practice using the command window:**

Using the command window, begin a diary file with the name "practice_diary". Then do the following:

1. Clear the workspace by typing the clear command.
2. Create a variable *b* and set it equal to 7
3. Create a variable *a* and set it equal to 4
4. Add *a* and *b* and assign the result as *x*
5. Subtract *a* and *b* and assign the result as y
6. Multiply *a* and *b* and assign the result as *z*
7. Divide *a* by *b* and assign the result as r
8. Find *b* to the power of *a* and assign the result as s
9. Use the up arrow key to go back to the the command from step 4. Edit the command to assign it as *v* istead of *x* and end the command a semicolon; What does the semicolon do?
10. End the diary
11. Clear the command window with clc

The workspace

Notice that your workspace now contains all variables you defined. The workspace should look like this:



You can save the variables in the workspace as a binary ".mat file" with the command:

```
save filename
```

Use the command window to save your workspace using the file name "practice_workspace.mat". Notice the new file shows up in

the **Current Folder Window**.

Now, clear the workspace with the clear command.

```
clear
```

Just for practice, use the load command to load the file you just saved and inspect the workspace:

```
load filename
```

Clear the workspace again before moving to the next section.

Discussion Questions15.2.1.1

1. Where was the practice_diary file saved and what extension does it have? How would you submit a file like this to Gradescope?
2. When mathematical operations are performed in the command window, how are they defined in the workspace? What happens to the previous value in the workspace when you enter a new operation? (eq, try a + b , then a^b)
3. What does a semicolon at the end of a command do?
4. What does a percentage sign at the beginning of a line do?

Practice with Script Files

The Command Window is convenient for quick operations that you don't want to save. But it has some big limitations. For example, even if you do save the diary, you can't re-run any of the commands automatically. A better way to save your work is by entering it in a Script File.

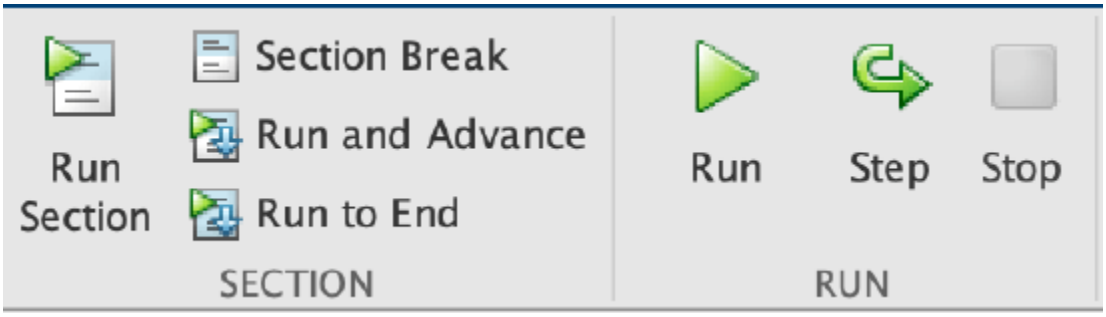
One way to start a new script is to go to the Home Tab and select **New**, then **Script**. Instead, let's use the command line to start a new script called "reference_script.m". Type the following into the command window:

```
edit reference_script.m
```

This will create a new script file. The new file should appear in the Current Folder window and it will open as a new tab in the Editor Window.

Find the Editor Window. In the Editor window, type the following:

```
%% Editor Exercises %%
% single percent sign indicates a text line
% double %% percent (only) indicates a section break.
% you can run each section of the editor by pressing the Run Section button.
% you can run the entire editor by pressing the Run button
```



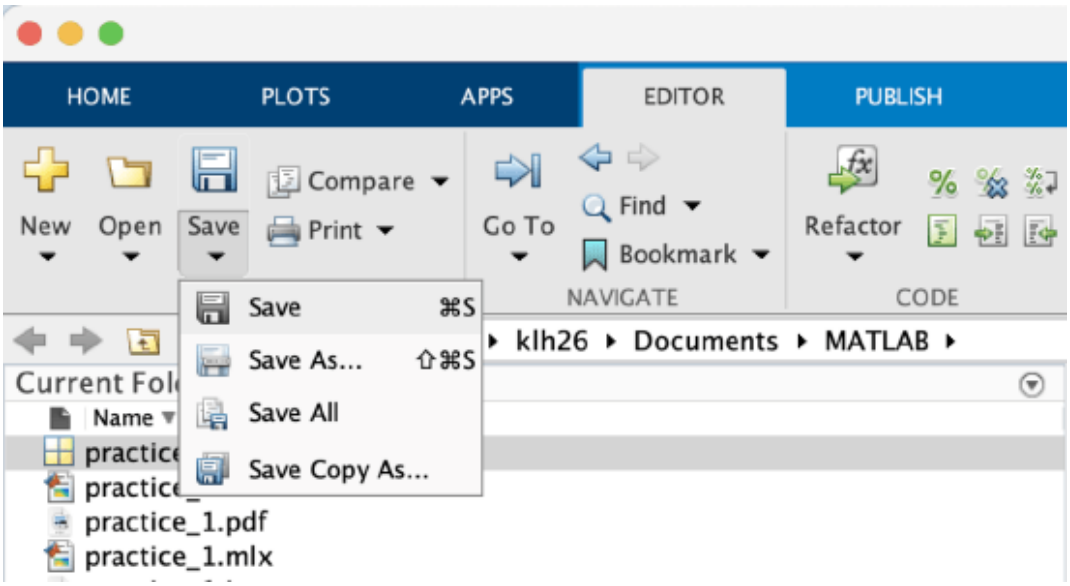

```
%%
%Type this into the new script in the Editor
b = 7
a = 4
```

```
% then hit run.
```

Notice what happens in the command window and in the workspace.

```
% again, type these examples of simple operations into the editor
x = a+b
y = a-b
z = a*b
r = a/b
s = b^a
% hit run and look at the command window
% then clear the command window and clear the workspace
% then add semicolons to the end of the lines and hit run again
```

Now that we see how the editor works, let's save the contents of the editor window as "reference_script.m". Go to the Editor tab and choose save.



At the end of the script that you just saved, add the following. Then run each section to see what happens. You can view any variables by typing their name in the command window.

```
%%
%% Building a reference sheet %%
a = 7;
b = 4;

%%
%Simple matrix - you can use spaces or commas to separate entries%
l = [1 2 3];
%%
%multiple rows - separated by semicolons%
m = [1;2;3];
%%
%matrices can have expressions in them%
n = [a+b, a-b, a*b];
%%
%transpose matrices with an apostrophe%
N = n';
%%
%multiply matrices
L = l*m;
M = m.*N;
```

```
%works the same with division
%%
%Create a matrix with regularly spaced intervals - defaults to one if not
%otherwise specified%
e = [1:16];
E = [1:0.5:16];
%%
%To reference specific elements of a matrix, call the matrix and then add
%coordinates (row, column) or just one number if it's a vector%
e7 = e(7);
m2 = m(2);
%%
%delete specific elements of a matrix
h = [1 2 3;4 5 6;7 8 9];
h(2) = [];
%check value of h in workspace
%%
%How to plot stuff
%you can just say "plot" but to intentionally keep track of figures it's a
%good idea to invoke figures by number
x = [1 2 3 4 5];
y = x.^2;
z = y./2;
figure(1)
hold on
plot(x,y)
plot(x,z,"o")
hold off
A = [1, 5, 0, 20];
axis(A)
xlabel('x')
ylabel('x^2')
title('Example')
%you can get help for any function you want to use (ex: plot()) by searching
%in the "Search Documentation" box at the top right of the screen
```

Save your files. Then clear the workspace and command windows before proceeding to the next section.

Discussion Questions15.2.1.2

1. What is the purpose of the period in the following statement? What happens if the period is removed?

   ```
   M = m.*N;
   ```

2. How can you delete the value 0.4 in the following matrix?

   ```
   mat1 = [0.1 0.2 0.3 0.4 0.5 0.9 1.0];
   ```

3. What does the "o" specification do in the code below:

   ```
   plot(x,z,"o")
   ```

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15.2.2: Practice with LiveScript

Install a custom script

The custom scripts (files with .m extension) and binary files (files with .mat extension) for this course are available here (click to go to GoogleDrive) using your Google account. If you are using the Chemistry Department *bohr* server to access Matlab, the scripts are already installed for you.

If you are using your own computer, the scripts and binary files should be added to the correct folder on your computer. Follow the instructions in this video to install the lsq script, which performs least squares analysis.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Practice using a custom script and a binary file

This is an exercise to give you some practice in using Matlab to analyze data provided in a binary file, and plot the results using a custom script for least squares analysis. Before you start, make sure the custom files lsq.m and expt-1.mat are in your working MatLab directory (see video above). The binary file "expt-1" simply contains pre-defined 80 x 1 vector matrixes "x" and "y". This is just to save you the hassle of typing in the values for each vector.

> Open the "Practice_LiveScript_XXX.mlx" file, and simply follow the instructions within the Live Script document.

The file linked above will walk you through the following steps to create a "final" plot.

1. Open the MatLab program and be sure that you are working in the directory containing the lsq script and expt-1 binary file.
2. Type the following: **load expt-1**
   Your workspace now contains two variables, x and y which obey the following relation:
$$y = Ae^{-Cx} \tag{15.2.2.1}$$
3. Plot y (ordinate) versus x (abscissa). Using Matlab, recalculate your data in linear form (ln y versus x) and plot the result. Using least squares analysis of the linearized data, calculate the values of A and C and report the standard deviation in these values. Using your calculated values of A and C, use Matlab to draw (a) the least-squares fitted line through your linear plot and (b) the best fit curve through your exponential plot. (NOTE: data should appear as points using the symbol 'o' and least squares fitted lines should be solid lines.)

   > **Expectation for a "final" full-credit plot in this course:**
   >
   > - Data is plotted in scatter format.
   > - Axes are correctly labeled, with correct units.
   > - When appropriate, a curve fit to the data is shown
   >   - equation of the line is shown on the plot, but not obscuring the data
   >   - uncertainty in slope and intercept provided

        - correlation coefficient (R) provided
    - Approrpate units are given for every value and every axis label.
    - Plot is centered on graph.
    - Text is easily readable (usually this means it is large enough to read easily.

4. You should show the plots described in (3) together with the values of A and C to your instructor. Each graph should have a title, and the x- and y-axes should be labeled.

This is an old video of this activity (before LiveScript files were developed.)

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

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15.2.3: MatLab for Data Analysis In This Course

MatLab is the preferred tool for data analysis in this course. That means that we will provide MatLab templates for your data analysis in each module and we can provide some basic support for your computational work if you use MatLab. However, if you have a favorite tool that is not MatLab, you are welcome to use it instead from now on, but please know that your instructional team may not be able to offer technical support for other computational programs.

We provide the MatLab Live Script files that can support your work in the modules this semester. Let's take a close look at the one for your "Error Analysis" problem set (your next assignment, in Module 3).

With any time remaining in the class meeting, or with your time out of class, access the MatLab files for this course and find the "Treatment of Error folder". From this folder, open the file called "Error_StudentGuide_date.mlx" and follow the instructions within to begin completing your next assignment. Also proceed to the next module (Module 3) in this manual to view the pre-lab assignment for your next meeting.

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15.3: HOW TO ACCESS MATLAB (DUKE STUDENTS)

There are several options for accessing Matlab at Duke:

Whichever option you choose, it is ideal if you stick with the same way of accessing MatLab for the duration of the semester so that all your files are available in the same place. Read the information below to understand your options.

1. **OPTION 1**: Use **MatLab Online using an internet browser.**
   There are specific limitations of the online version of MatLab, but for the purposes of this course, MatLab Online is a convinient option. You have free access to MatLab online using your Duke Login Credentials.
   *__NOTE:__ *Visiting students may be excluded from this access, so make sure you check your access asap if you are a visiting student at Duke)*
2. **OPTION 2**: You can **download and install software onto your own computer** to access Matlab.
   a. **Install Matlab on your own computer.** Installing the Matlab program on your own computer will likely give you a faster response, but the Matlab software will take up as much as six gigabytes (6GB) of space on your hard drive.
   b. **OR...Use the emulation software, FastX** to access the Matlab installed on the chemistry department "bohr" server. FastX exists in a web browser version, or you can download it onto your computer. However, running a remote connection from your computer to bohr can result in a slower response since the speed will be related to the speed of your network connection. Additionally, you will have to get copies of our in-house scripts and place them in the MatLab path so that they can be used when needed. You will also need the Duke VPN if you are off campus Instructions for both options are given in sections of this Module.
3. **OPTION 3**: You can access the MatLab program **using a lab computer.** However, MatLab is not installed on the lab computer hard drive. Rather, you can access the software that is installed on the chemistry department server (bohr) using an emulation software (FastX).
   - FastX is already installed on all laboratory computers in our P-Chem lab, and you are permitted to use those computers any time that the labs are open.
   - Alternatively, use a lab computer to access MatLab Online.

The ability to access MatLab from your own computer will allow you to do your data analysis without having to come in to the lab, therefore options 1 and 2 are recommended. Option 1 has the additional benefit of cloud backups of your work.

15.3.1: Install Matlab on your own computer

15.3.2: Access MatLab Remotely Through FastX

15.3.2.1: Transferring Files Between Your Computer and Your Duke NetID Account

15.3.2.2: Access from off-campus (The Duke VPN)

15.3.3: Invoking Matlab From the Lab Computers

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15.3.1: Install Matlab on your own computer

Another way access MatLab is to download and install the software on your own computer. The MatLab software with the additional "toolboxes" will take approximately 4 GB of space on your computer. If you have enough space on your computer to operate this software you can find instructions for downloading and installing the software at the links below.

- Duke OIT's Software List: https://software.duke.edu/
- Duke MatLab Portal: https://www.mathworks.com/academia/tah-portal/duke-university-30359028.html

If the links above are not working, try to search "Duke MatLab" on an internet browser and you will find the most recent information. (And please inform your instructors of any dysfunctional links!)

Additional Installation Instructions

During the installation of the software, it will be most convenient if you select to also install the following toolboxes in the PRODUCTS screen of the MatLab Installer (See image below).

- Curve Fitting
- Statistics and Machine Learning
- Symbolic Math

If you forget to do this, it can be done later through the Apps Tab in MatLab.

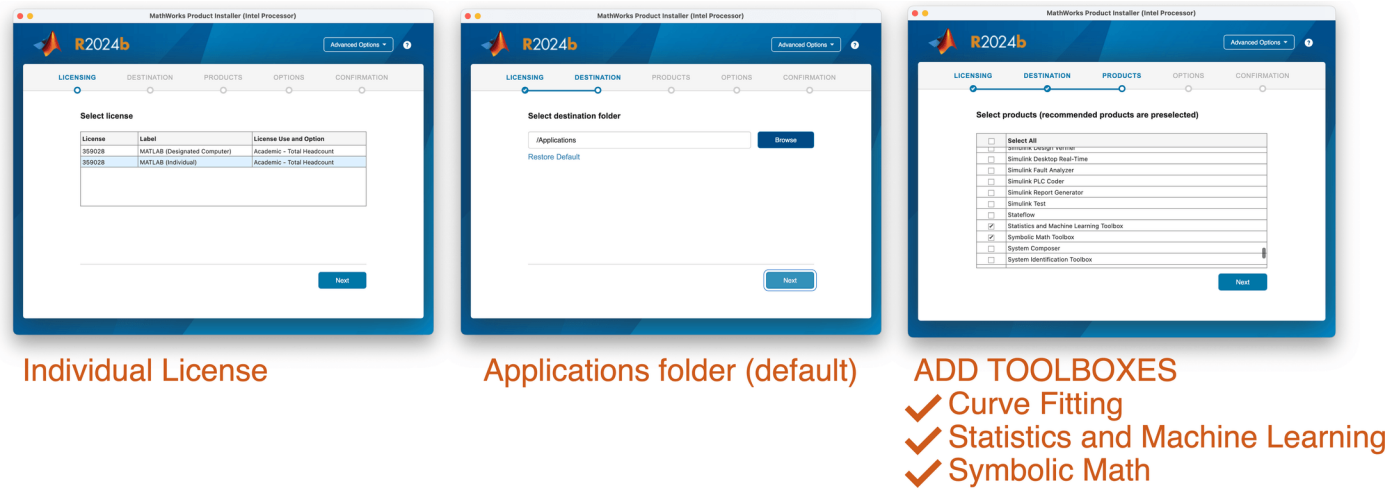


Figure 15.3.1.1: MatLab Install options. (Kathryn Haas; CC-NC-BY-SA)

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15.3.2: ACCESS MATLAB REMOTELY THROUGH FASTX

Use FastX to Access Software

This document describes two ways to access the server versions of Matlab, and later in the semester Spartan, from your own computer. These programs are housed on a chemistry server called bohr (at bohr.chem.duke.edu). You can access this server either by downloading and installing FastX; or, you can access bohr directly from your web browser. Both options are described below

Option 1: Download and Install FastX on Your Computer:

1. Copies of both the Windows and Macintosh Installers are available from the Software section of the OIT web site, www.oit.duke.edu/software. Download and install the appropriate one for your computer. Installation is quick and straightforward, just follow the prompts.



2. Once installed, Launch the program from the icon.

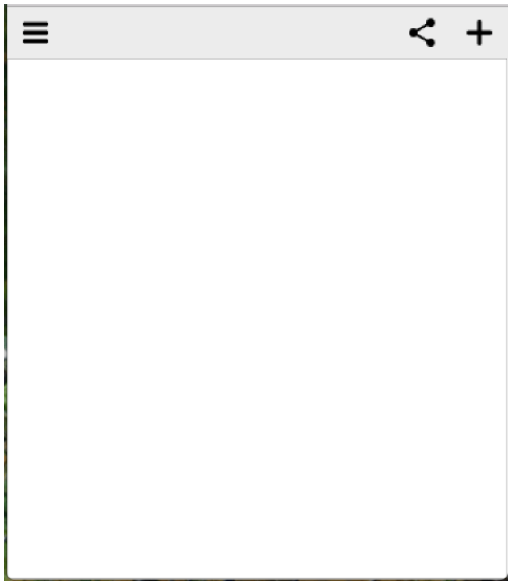


Figure 15.3.2.1: Configuring FastX. (CC-NC-BY-DUKE CHEM)

3. Click on the + sign at the upper right of the main window. Select SSH from the menu that appears.
4. Complete the New SSH connection box as follows:

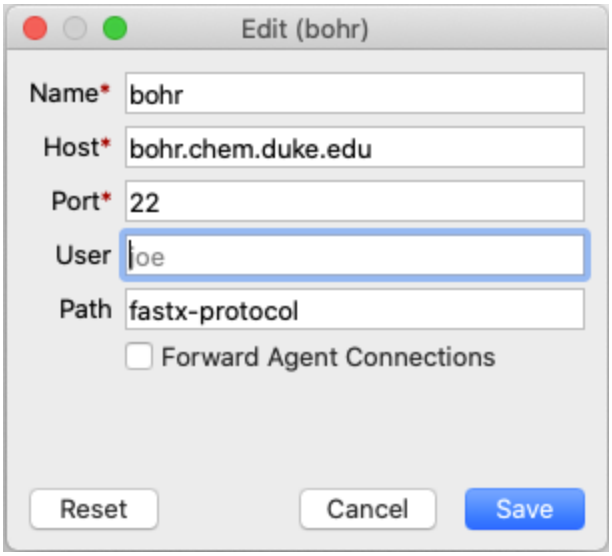


Figure 15.3.2.2: bohr.chem.duke.edu. (CC-NC-BY-DUKE CHEM)

For Name, call it Bohr, or really anything you want. For Host, enter bohr.chem.duke.edu. The Port should be 22. Enter your NetID username in the User box. The Path box should already be correct. Click on the Save button when done. The program will attempt to connect to bohr.chem.duke.edu. If you get a message saying the system is not recognized by this computer (or something to that effect), click Continue. When prompted, enter your NetID (if you didn't add it to the connections setup box) and password.

5. Click on one of the xterm choices from the new window that appears.



Figure 15.3.2.3: Choose xterm. (CC-NC-BY-DUKE CHEM)

6. An x-terminal window will open. At the prompt type,

```
matlab
```

Option 2: Use FastX directly from a web browser:

1. Open a browser. We suggest using Chrome or Firefox, but likely any browser will work.
2. Navigate to https://bohr.chem.duke.edu:3300

When Prompted enter your NetID Username and Password

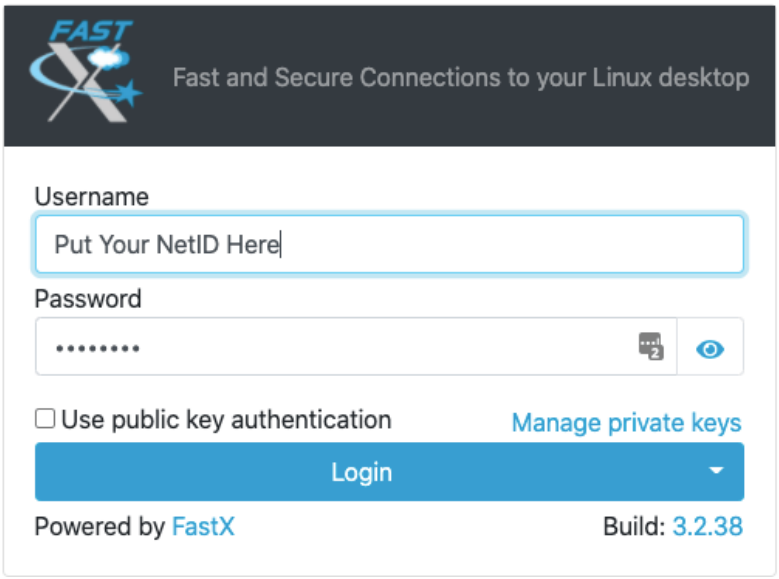


Figure 15.3.2.4: FastX Login From Web Browser. (CC-NC-BY-DUKE CHEM)

3. Click on the blue + at the top left of the next screen.

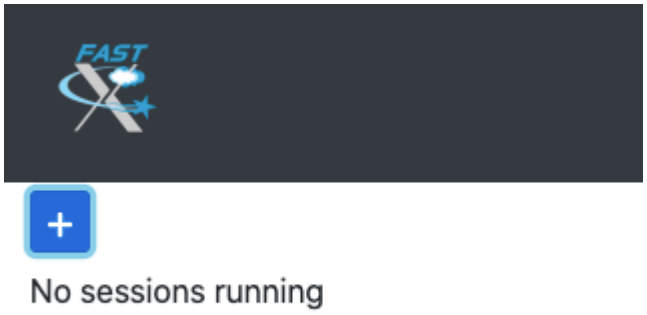


Figure 15.3.2.5: The New Session Button. (CC-NC-BY-DUKE CHEM)

4. Select xterm from the options on the next screen. Click Launch to start the session.

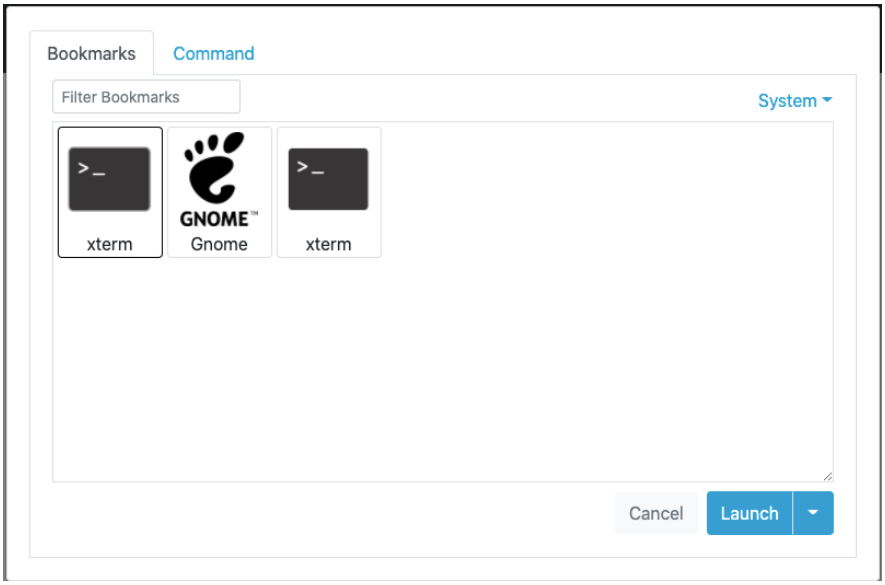


Figure 15.3.2.6: Launch a new Xterm Session. (CC-NC-BY-DUKE CHEM)

When your xterminal window appears, type,

```
matlab
```

at the prompt.

15.3.2.1: Transferring Files Between Your Computer and Your Duke NetID Account

15.3.2.2: Access from off-campus (The Duke VPN)

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15.3.2.1: Transferring Files Between Your Computer and Your Duke NetID Account

In several experiments this semester, you will use a lab computer for instrument control and data acquisition. There are times when it is convenient to have your raw data files uploaded to bohr so that you might analyze the data using Matlab. Additionally, there are times when files and figures (graphs) that are generated by matlab need to downloaded to your own computer. These operations can be done in the following manner.

1. To upload files from one of the lab computers to your online account:

1.1. Click on the 

icon found on the computer desktop to start the WinSCP file transfer program. The File protocol should be SFTP, and the port should be 22. Enter login.oit.duke.edu under Host Name. Enter your NetID (User name) and password, and click on Login. Click Continue at the Authentication Banner.

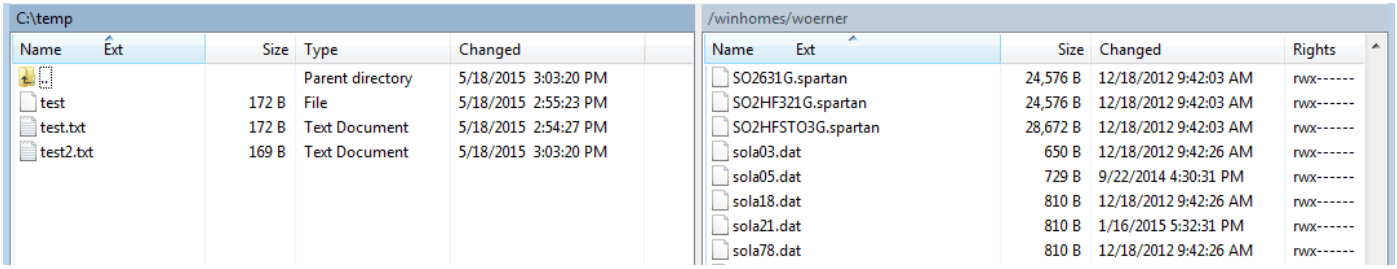
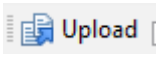


Figure 15.3.2.1.1: The Main WinSCP Window. (CC-NC-BY-DUKE CHEM)

1.2. You will see a dialog box, part of which is shown above. On the left-hand side of the screen is your local directory (i.e., the directory of the lab computer). It should default to the directory containing your data. If not, change the directory to the correct one. You should see a list of those files found in the local directory. On the right-hand side you will see the contents of your OIT account.

1.3. To transfer files from the local PC to your OIT account, first highlight the appropriate files you want transferred. Click on the 

button at the top of the screen. An Upload dialog box will appear. Click OK to copy your files from the local PC to your OIT account. Or, click on Transfer Settings if you want to check to see that the transfer is configured properly. (In general, the Transfer mode should be Text and the File modification should be No change.) Then click on **Copy**. Check to be sure all of your files are transferred and then exit your session by clicking the X at the upper right corner of the screen.

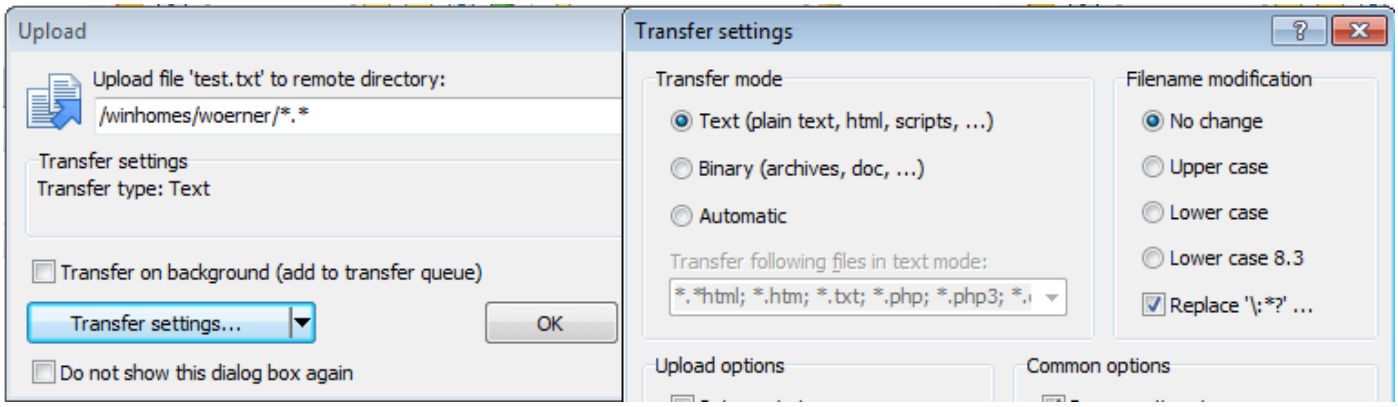


Figure 15.3.2.1.2: The WinSCP Upload Screen. (CC-NC-BY-DUKE CHEM)

2. **Downloading** files from your OIT account to your own **Windows** computer or to one of the lab computers is accomplished in the same manner, except that you should select the files you want to download, and execute the transfer from your OIT account to your local computer.

3. **Transferring** files back and forth between your **Macintosh** computer and your OIT account can be accomplished in the following manner.

3.1. From the Go menu (found when you are in your Finder), select **Connect to Server**.



Figure 15.3.2.1.3: The Macintosh Go Menu. (CC-NC-BY-DUKE CHEM)

3.2. In the text box at the next screen enter,

`smb://homedir.win.duke.edu/users/`*`the first letter of your NetID/your full NetID`*

An example of a correct server address is shown below, where w is the first letter of the NetID, and woerner is the NetID.

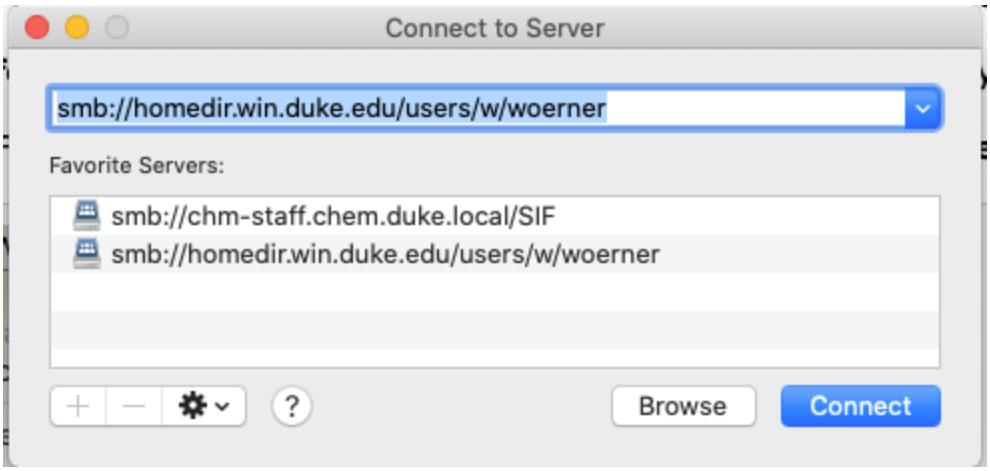


Figure 15.3.2.1.4: The Connect to Server Screen. (CC-NC-BY-DUKE CHEM)

3.3. Click the **Connect** button. You will be prompted for your NetID and Password.

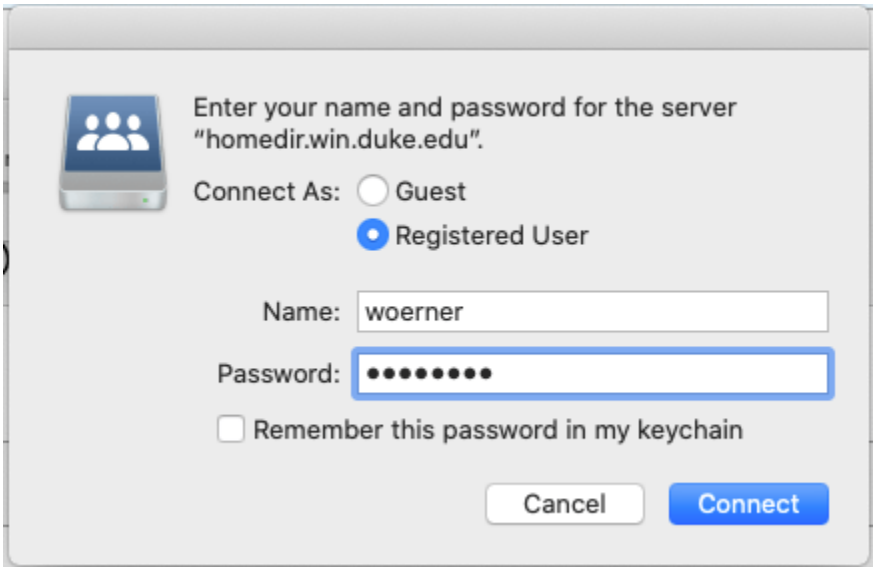


Figure 15.3.2.1.5: Login Screen. (CC-NC-BY-DUKE CHEM)

3.4. Once connected a new icon will appear on your desktop.



Figure 15.3.2.1.6: The Connectred Server Icon. (CC-NC-BY-DUKE CHEM)

If you do not see the icon appear, Check the **Finder Preferences**,

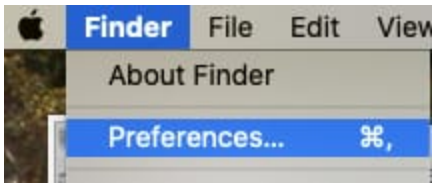


Figure 15.3.2.1.7: The Finder Menu. (CC-NC-BY-DUKE CHEM)

and make sure Connected Servers is checked.

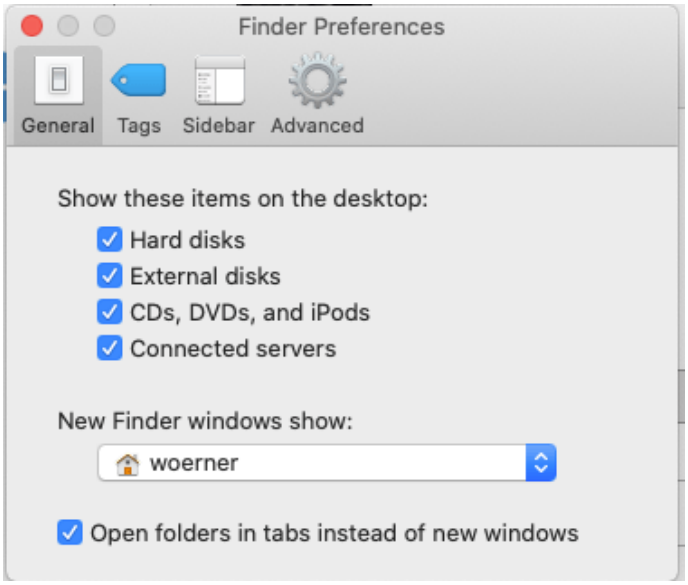


Figure 15.3.2.1.8: Finder Preferences. (CC-NC-BY-DUKE CHEM)

3.5. The connected server on your desktop acts like any other folder on your Mac. Click on it to open it and see the contents of your online OIT account. Drag and drop to move files back and forth between your Mac and your OIT account.

This page titled 15.3.2.1: Transferring Files Between Your Computer and Your Duke NetID Account is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn Haas.

15.3.2.2: Access from off-campus (The Duke VPN)

If you are planning to access Matlab, or later in the semester Spartan, from an off-campus location you will need to install and run the Duke **V**irtual **P**rivate **N**etwork (VPN) software. Complete instructions for downloading, installing, and running the Duke VPN software can be found here:

For Windows computers.

For Macintosh computers.

Remember to start the VPN before accessing Matlab (or Spartan) from an off-campus location.

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15.3.3: Invoking Matlab From the Lab Computers

INVOKING MATLAB FROM COMPUTERS IN THE LABS

1. To start Matlab on any of the computers in the lab:



FastX

1. Click on the FastX icon, on the main desktop screen, and then on the bohr.chem.duke.edu session. Enter your NetID and password and click OK. Once logged in, click on the + in the upper right of the bohr.chem.duke.edu window.

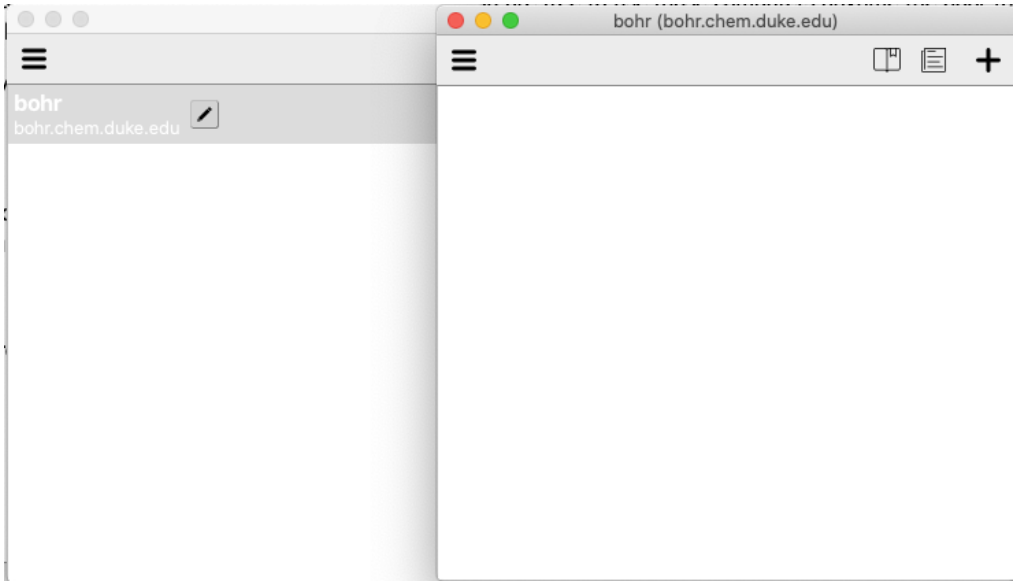


Figure 15.3.3.1: Connecting to Bohr through FastX. (CC-NC-BY-DUKE CHEM)

2. Click on one of the xterm choices from the new window that appears.



Figure 15.3.3.1: Choose xterm. (CC-NC-BY-DUKE CHEM)

3. An x-terminal window will open. At the prompt type,

```
matlab
```

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15.4: USING MATLAB (SUPPLEMENTAL)

> If you are a brand new Matlab user, or its been a long time since you've used it, the "hopw-to" sections of this manual may seem opaque. A great way to start it to run through the "Getting Started" tutorials from Matlab.

We will introduce you to using Matlab to perform numeric calculations. If you wish, you may save a copy of your work for printing later. This is done using the **diary** command, which captures a copy of all subsequent keyboard input and most of the resulting output (with the exception of graphs) to be written to a named file. If the file already exists, the output is appended to the end of the file. For example, the command,

```
diary exptA
```

will save your work in the file exptA. This file can be downloaded to your computer for later use as described in section 1.2.15. When you have completed your work, the command,

```
diary off
```

will suspend the diary.

> **IMPORTANT NOTE:**
>
> The diary command merely "records" your on-screen work. It does not save your data. Data must be saved as described in Section 1.2.12. Although diary files may be printed, they cannot be retrieved for viewing on the screen.

15.4.1: Entering Matricies

15.4.2: Matrix Computation

15.4.3: Vectors

15.4.4: Subscripting

15.4.5: Finding, Deleting, Adding or Replacing Data

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15.4.8.1: Array Addition and Subtraction

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15.4.9.3: Multiple Plots

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15.4.10: Linear Least Squares Analysis
15.4.11: Last Line Editing and Recall
15.4.12: Saving Data
15.4.13: Deleting Matrices
15.4.14: Quitting Matlab
15.4.15: Transferring Files Between Your Computer and Your Duke NetID Account

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15.4.1: Entering Matricies

Matlab works with essentially only one kind of object, a rectangular numerical matrix. In some situations, special meaning is attached to 1-by-1 matrices, which are scalars, and to matrices with only one row or column, which are vectors.

Matrices can be introduced into Matlab in several different ways. The easiest method for small matrices is to use an explicit list. The explicit list is surrounded by square brackets, and uses the semicolon, ; , to indicate the ends of the rows. For example, to enter a 3-by-3 matrix, we type:

```
A = [1 2 3; 4 5 6; 7 8 0]
```

This results in the output

A =

1 2 3
4 5 6
7 8 0

The matrix A is saved for later use. The individual elements in the input should be separated by commas or blanks and can be any Matlab expression. For example, typing

```
x = [-1.3, 4/5, 4*atan(1)]
```

uses Matlab like a calculator and results in

x =

-1.3000 0.8000 3.1416

Matrices entered, horizontally, as shown above, can sometimes be long enough to require more than one line. Matlab must be told when a wrap to another line is wanted. To do this, as you near the end of the line, add a space (spacebar) followed by three periods (...). Then hit enter. You will be allowed to continue entering numbers into the same matrix on the new line. Alternatively, if entering matrices horizontally is troublesome, you can always enter numbers vertically.

Typing:

```
y = [1
2
3
4
5]
```

results in:

y=

1

2

3

4

5

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15.4.2: Matrix Computation

We will run through some basic matrix operations. Operations and commands in Matlab are intended to be natural, in a matrix sense, not unlike how they might be indicated on paper. For example, our matrix A can be transposed with:

```
B = A'
```

which results in:

```
B =

1 4 7
2 5 8
3 6 0
```

Transposing x,

```
x = x'
```

results in:

```
x =

-1.3000
0.8000
3.1416
```

Matrix multiplication is indicated with:

```
C = A * B
```

producing:

```
C =

14 32 23
32 77 68
23 68 113
```

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15.4.3: Vectors

Vectors with regularly spaced elements may be generated using the colon:operator.

The statement

```
D = 1:4
```

results in

D =

1 2 3 4

Two colons may be used to create vectors with increments between the elements. Typing:

```
E = 0:0.1:0.5
```

results in

E =

0.0000 0.1000 0.2000 0.3000 0.4000 0.5000

Vectors are used often in Matlab because of the ease with which they allow data manipulation and function evaluation. When a function is applied to a vector in Matlab, the function is applied to each element of the vector. For example, consider taking the sine of the four elements in vector D above. Typing:

```
Y = sin(D)
```

results in

Y =

0.8415 0.9093 0.1411 –0.7568

A wide variety of data analysis functions are available that operate on vectors. Typical functions include cumulative sum,

```
cumsum(Y)
```

ans =

0.8415 1.7508 1.8919 1.1351

mean and standard deviation,

```
m = mean(Y), s = std(Y)
```

m =

0.2838

s =

0.7758

Other useful functions include:

max(x)	returns the largest element in the vector x
min(x)	returns the smallest element in the vector x
median(x)	returns the median value of the vector x
sort(x)	sorts the elements of x in ascending order
sum(x)	returns the sum of the elements of x

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15.4.4: Subscripting

Enclosing their subscripts in parentheses may reference individual matrix elements. The statement A(m,n) refers to the mth row, and nth column, of matrix A. For example, given a matrix A:

```
A =

1 2 3
4 5 6
7 8 9
```

the statement

```
A(3,3) = A(1,3) + A(2,2)
```

results in

```
A =

1 2 3
4 5 6
7 8 8
```

A subscript can be a vector. If X and V are vectors, then X(V) is [X(V(1)), X(V(2)), ..., X(V(n))]. For matrices, vector subscripts allow access to contiguous and noncontiguous submatrices. For example, suppose that A is a 10-by-10 matrix. Then,

```
A(1:5,3)
```

specifies the 5-by-1 submatrix, or column vector, that consists of the first five elements in the third column of A. Similarly,

```
A(1:5,7:10)
```

is the 5-by-4 submatrix of elements from the first five rows and the last four columns.

Using the colon by itself in place of a subscript denotes *all* of the corresponding row or column. For example,

```
A(:,3)
```

is the third column and

```
A(1:5,:)
```

is the first five rows.

In general, if v and w are vectors with integer components, then

```
A(v,w)
```

is the matrix obtained by taking the elements of A with row subscripts from v and column subscripts from w.

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15.4.5: Finding, Deleting, Adding or Replacing Data

The following examples will illustrate how to find, change, add or delete data in a vector. The same principles apply to manipulation of data in matrix form.

(a) Finding Data:

Suppose we wish to find the elements of vector V which are greater than or equal to 7:

```
V = [-2 3 7 -26 48 10 -8]', i = find(V>=7)
```

results in

V =

-2

3

7

-26

48

10

-8

i =

3

5

6

The statement, i = find(V>=7), returns a vector, i, containing the index of the elements of V which are greater than or equal to 7. The third, fifth and sixth elements of V are ≥ 7.

There are six relational operators that can be used in Matlab:

Relational Operators

< less than

<= less than or equal to

> greater than

>= greater than or equal to

== equal to

~= not equal to

(b) Deleting Data:

Specific elements in a matrix or vector can be deleted using the empty matrix (or vector), []. The statement

```
x = []
```

assigns a matrix of dimension zero-by-zero to x. To delete the elements of V which are greater than or equal to seven, use the command

```
V(i) = []
```

which returns

V =

-2

3

-26

-8

The elements of V which have indices given by the elements of i, are removed by assigning them to an empty matrix. Single elements may be removed in similar fashion. The command

```
V(3) = []
```

deletes the third element of V and returns

V =

-2

3

-8

An efficient way of removing rows and columns of a matrix is to assign them to an empty matrix. The command, **A(:,3)=[],** deletes column 3 of matrix A.

(c) Adding Data:

Suppose we wish to combine the elements of vectors V and U:

```
U = [3:2:10]', W = [V; U]
```

This returns

U =

3

5

7

9

W =

-2

3

-8

3

5

7

9

If we wish to add a single data point (-17) to the end of vector W:

```
W = [W; -17]
```

This returns

W =

-2

3

-8

3

5

7

9

-17

(d) Replacing Data:

To replace the fourth element of W with -12, enter the following

```
W(4) = -12
```

This returns

W =

-2

3

-8

-12

5

7

9

-17

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15.4.6: Output Format

The result of any Matlab assignment statement is displayed on the screen, as well as assigned to the specified variable or to **ans** if no variable name is given. The numeric display format can be controlled using the **format** command. **format** affects only how matrices are displayed, not how they are computed or saved (Matlab performs all computation in double precision).

If all the elements of a matrix are exact integers, the matrix is displayed in a format without any decimal points. For example,

```
x = [-1 0 1]
```

always results in

x =

-1 0 1

If at least one of the elements of a matrix is not an exact integer, there are several possible output formats. The default format, called the **short** format, shows approximately 5 significant decimal digits. The other formats show more significant digits or use scientific notation. As an example, suppose

```
x = [4/3 1.2345e-6]
```

The formats, and the resulting output for this vector, are:

format short

1.3333 0.0000

format short e

1.3333E+000 1.2345E-006

format long

1.33333333333333 0.00000123450000

format long e

1.333333333333333e+00 1.234500000000000e-06

For the long formats, the last significant digit may appear to be incorrect, but the output is actually an accurate decimal representation of the binary number stored in the computer.

With the short and long formats, if the largest element of a matrix is larger than 1000 or smaller than 0.001, a common scale factor is applied to the entire matrix when it is displayed. For example,

```
x = 1.e20*x
```

multiplies x by 1020 and results in the display

x =

1.0E+020 *

1.3333 0.0000

One final command, **format compact**, suppresses many of the line-feeds that appear between matrix displays and allows more information to be shown on the screen.

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15.4.7: The Help Facility

A HELP facility is available, providing online information on most Matlab topics. To get a list of HELP topics, type

```
help
```

To get HELP on a specific topic, type help **topic**. For example,

```
help eig
```

provides HELP information on the use of the eigenvalue function,

```
help []
```

tells how to use brackets to enter matrices, and

```
help help
```

is self-referential, but works just fine.

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15.4.8: ARRAY OPERATIONS

We use the term **array operations** to refer to element-by-element arithmetic operations, instead of the usual linear algebraic matrix operations denoted by the symbols * / \ ^ '. Preceding an operator with a period **.** indicates an array or element-by-element operation.

15.4.8.1: Array Addition and Subtraction

15.4.8.2: Array Multiplication and Division

15.4.8.3: Array Powers

15.4.8.4: Math Functions

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15.4.8.1: Array Addition and Subtraction

For addition and subtraction, the array operations and the matrix operations are the same, so + and - can be regarded as either matrix or array operations.

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15.4.8.2: Array Multiplication and Division

Array, or element-by-element, multiplication is denoted by **.***. If **A** and **B** have the same dimensions, then **A .* B** denotes the array whose elements are simply the products of the individual elements of **A** and **B**. For example, if

x = [1 2 3]; y = [4 5 6];

then,

```
z = x.*y
```

results in

z =

4 10 18

X = A./B is a solution to X.*B = A and X = A.\B is a solution to A.*X = B so, the expressions A./B and A.\B give the quotients of the individual elements.

```
z = x.\y
```

results in

z =

4.0000 2.5000 2.0000

To obtain the reciprocal of the elements of x, type

```
w = x.\1
```

This results in

w =

1.0000 0.5000 0.3333

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15.4.8.3: Array Powers

Element-by-element powers are denoted by **.^**. Here are several examples, using the above vectors x and y. Typing

```
z = x.^y
```

results in

```
z =

1 32 729
```

The exponent can be a scalar.

```
z = x.^2
```

```
z =

1 4 9
```

Or, the base can be a scalar.

```
z = 2 .^x
```

```
z =

2 4 8
```

Note

This last example illustrates one of Matlab's syntactic subtleties. Although it is difficult to see, the space between the digit 2 and the period **.** is important. If it were not there, the period would be interpreted as a decimal point associated with the 2. An alternative to the space is to use parentheses, forcing the correct precedence.

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15.4.8.4: Math Functions

Available math functions include the following:

MATH FUNCTIONS

Use the Help command to obtain further information on any of these functions

abs	absolute value or complex magnitude
sqrt	square root
real	real part
imag	imaginary part
round	round to nearest integer
exp	exponential base e
log	natural logarithm
log10	log base 10
sin	sine
cos	cosine
tan	tangent
asin	arcsine
acos	arccosine
atan	arctangent

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15.4.9: GRAPHICS

One of the major advantages of Matlab is its graphics capability. The graphics commands are natural and easy-to-use, yet still succinct, powerful, and extensible.

Scientific and engineering data are examined graphically in Matlab by using a "graph" command to create a plot on the screen. There are seven different types of "graph" from which to choose:

GRAPH

plot linear X-Y plot
loglog loglog X-Y plot
semilogx semi-log X-Y plot (x-axis logarithmic)
semilogy semi-log X-Y plot (y-axis logarithmic)
polar polar plot
mesh 3-dimensional mesh surface
contour contour plot

The **plot** command creates linear X-Y plots. Once the plot command is understood, logarithmic and polar plots are created by substituting the commands **loglog**, **semilogx**, **semilogy**, or **polar** for **plot**. All five commands are used the same way; they only affect how the axis is scaled and the data are displayed.

15.4.9.1: Basic Plots

15.4.9.2: Line Types

15.4.9.3: Multiple Plots

15.4.9.4: Manual Axis Scaling

15.4.9.5: Overlaying Plots

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15.4.9.1: Basic Plots

If Y is a vector, plot(Y) produces a linear plot of the elements of Y versus the index of the elements of Y. For example, suppose we would like to plot the numbers {0., .48, .84, 1., .91, .6, .14}. This is quickly accomplished by typing

```
Y = [0. .48 .84 1. .91 .6 .14];
plot(Y)
```

which results in a graph on the screen:

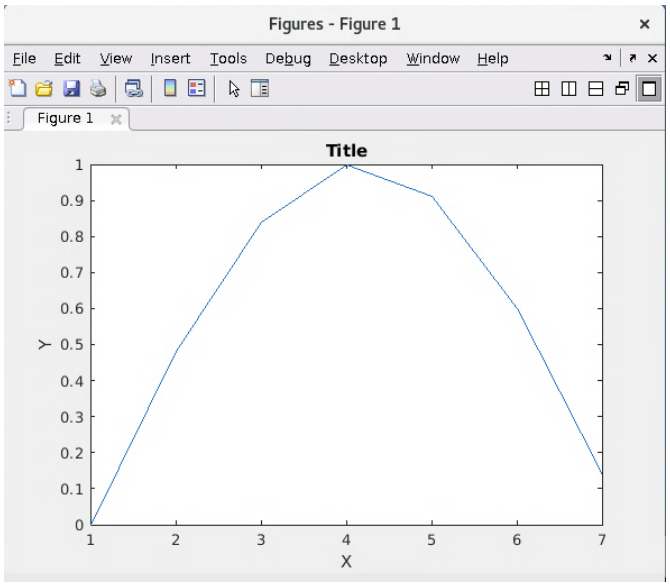


Figure 15.4.9.1.1: A Basic Plot. (CC-NC-BY-DUKE CHEM)

Notice that the data are auto-scaled and x- and y-axes are drawn. Use X Label; Y Label; and, Title from the Insert Menu to add a title and axes labels to your graph. Or, select Property Editor from the View menu. A Properties Editor box appears from which you can enter axes labels, a title and etc.

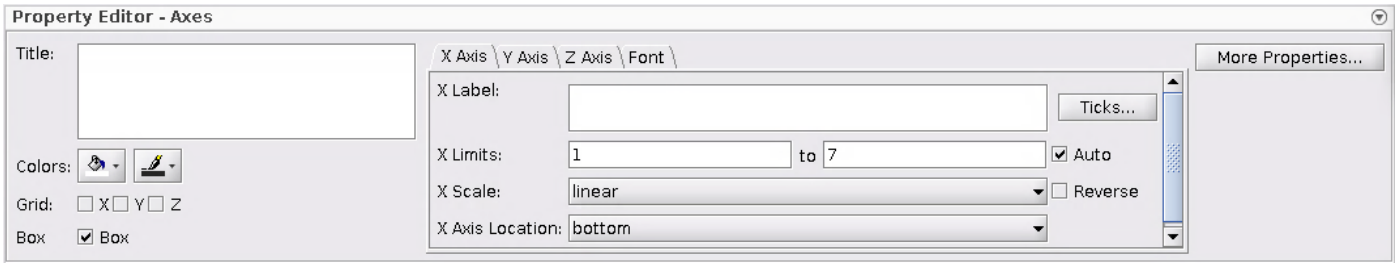


Figure 15.4.9.1.2: Property Editor. (CC-NC-BY-DUKE CHEM)

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15.4.9.2: Line Types

(b) Line types

The line types used on a graph may be controlled if the defaults are not satisfactory. Typically one does not connect data points with a line. Point plots using various symbols may be selected directly in the plot command. For example,

```
plot(X,Y,'x')
```

draws a point plot using x-mark symbols while

```
plot(X1,Y1,':',X2,Y2,'+')
```

uses a dotted line for the first curve and the plus symbol + for the second curve. Create vectors X1, Y1, X2 and Y2 and try this! Other line and point types are:

Line Type	Point Type
solid -	point .
dashed --	plus +
imag	imaginary part
dotted :	star *
dashdot -.	circle o
	x-mark x

Alternatively, the line type can be modified from within the Properties Editor window after the plot command is issued. Working with the graph above, with the Properties Editor window open, first select the arrow tool . Then click once somewhere on the actual data points. The data set will be highlighted and the Properties Editor window will change to display line properties. Under the Line menu select no line, and choose a marker from the Marker menu.

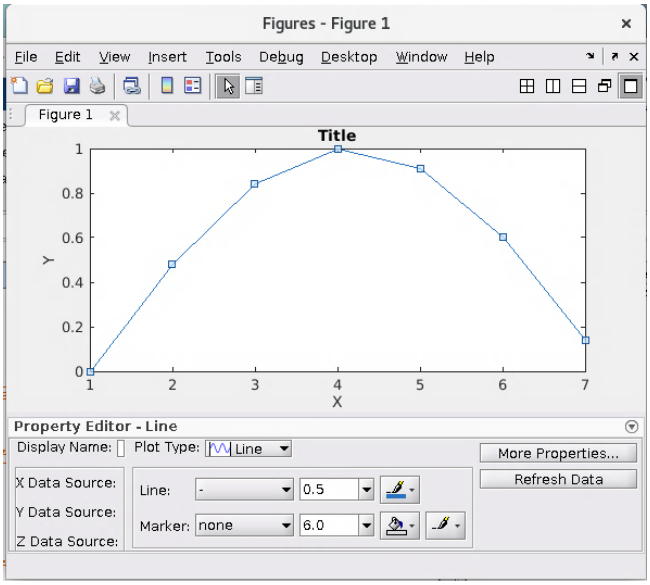


Figure 15.4.9.2.1: Line Editor.

Your graph will change accordingly. Finally, selecting More Properties from the Property Editor opens an additional options box.

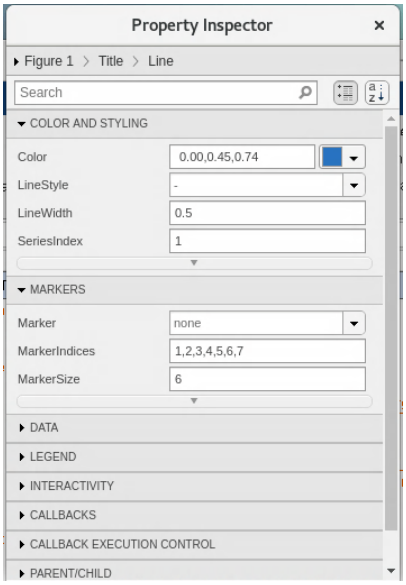


Figure 15.4.9.2.2: Property Inspector.

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15.4.9.3: Multiple Plots

The way to plot multiple lines on a single graph is to use plot with multiple arguments:

```
plot(X1,Y1,X2,Y2,...,Xn,Yn)
```

The variables X1,Y1, X2,Y2 etc. are pairs of vectors. Each x-y pair is graphed, generating multiple lines on the plot. Multiple arguments have the benefit of allowing vectors of differing lengths to be displayed on the same graph. Each pair uses a different linetype.

We can apply what we learned in the previous sections to plot simple functions. For example, to examine the behavior of the functions sin(x) and x2/100 on the interval from -15 to 15:

```
x = -15:.05:15;
y = sin(x);
z = x.^2/100;
plot(x,y,x,z)
```

which results in:

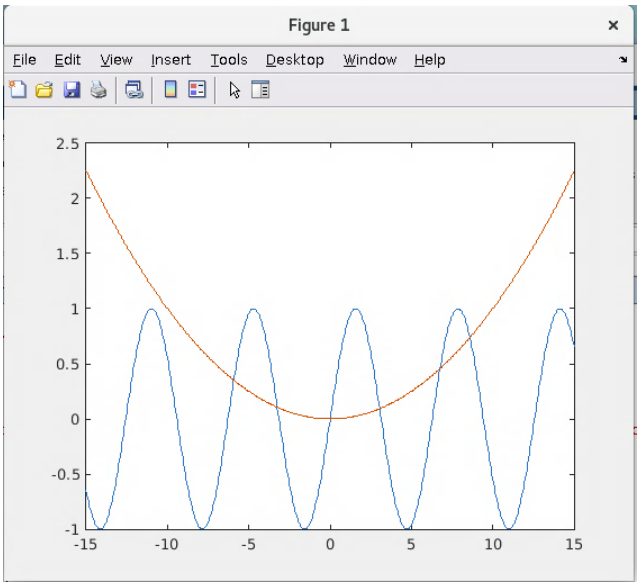


Figure 15.4.9.3.1: Multiple Plots.

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15.4.9.4: Manual Axis Scaling

In certain situations, it may be desirable to override the automatic axis scaling feature of the plot command and manually select the axis limits. Manual axis scaling is easily accomplished from the Properties Editor window mentioned above.

Alternatively, manual Axes Scaling can be accomplished from the Matlab workspace by creating a vector, V, with the following configuration

V=[X-min, X-max, Y-min, Y-max]

Working from the example graph above, let's say you wanted to scale the X axis from –5 to 5 and the Y axis from –1.5 to 1.5. Enter the following:

```
V = [-5, 5, -1.5, 1.5]
axis(V)
```

Retype the plot command plot(x,y,x,z) to observe the rescaled graph. The command **axis(V)** sets the axis scaling to the prescribed limits. If you reenter the command:

```
axis
```

autoscaling is resumed. Again, retype the command, plot(x,y,x,z), to observe the graph.

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15.4.9.5: Overlaying Plots

The command,

```
hold
```

holds the current graph on the screen. Subsequent plot commands will add to the graph, using the established axis limits and retaining the previously plotted curves. **hold** remains in effect until this command is issued again (i.e. the command **hold** can be "toggled" on and off).

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15.4.10: Linear Least Squares Analysis

To fit a straight line, y = mx + b, to a set of experimentally determined points

(x 1,y 1), (x 2,y 2), ..., (x n,y n) contained in the vectors [x] and [y], use **Basic Fitting** under the **Tools** menu in your graph window. Try this using the following data:

```
x = [-3.8 -1.2 0.75 3.1 5.6 8];
y = [8.2 6 3.3 1.6 -2 -6];
```

Selecting Basic Fitting from the Tools menu opens up an options box. Select **linear** as the fit type and choose how many significant figure you want in the calculation. A Linear Least-Squares line will be placed on the graph along with the equation for the line.

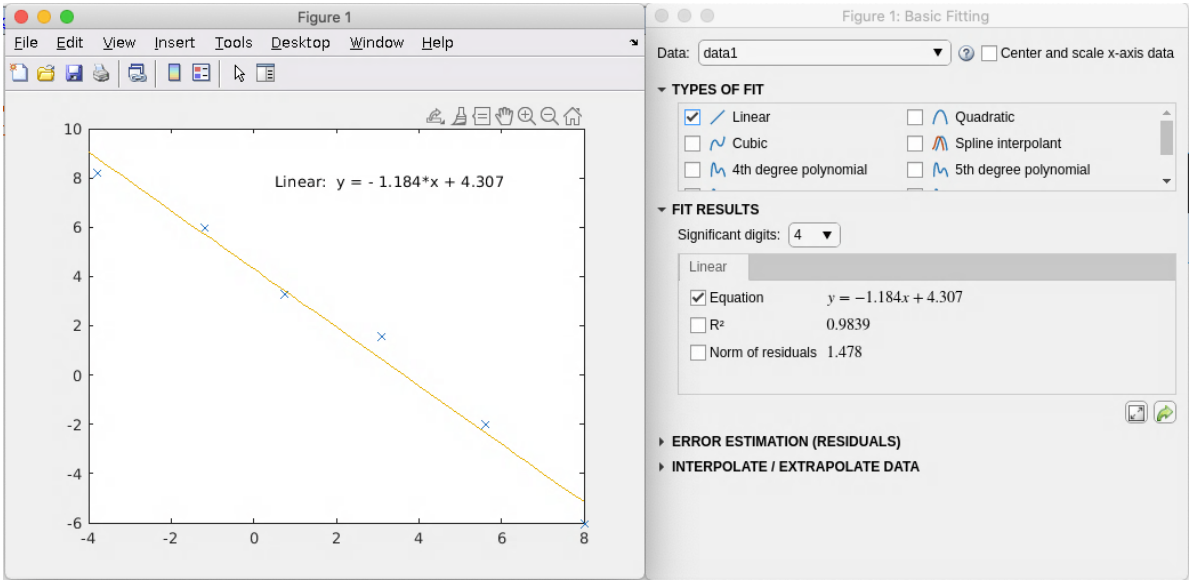


Figure 15.4.10.1: Basic Linear Fit. (CC-NC-BY-DUKE CHEM)

NOTE: Often for our purposes in the Physical Chemistry Laboratory it is often important to know the uncertainties (or standard deviation) in the calculated slope and intercept. To obtain calculated values of the slope, intercept, correlation coefficient along with the uncertainties in slope and intercept, use the **lsq** command. Using the current x,y data as an example, typing:

```
lsq(x,y)
```

returns the following:

```
>> x=[-3.8 -1.2 .75 3.1 5.6 8];
>> y=[8.2 6 3.3 1.6 -2 -6];
>> plot(x,y)
>> lsq(x,y)
        ***********************************************************************
                Slope =  -1.1839
                Y Intercept =   4.3066
                Standard Deviation of Slope = 0.075611
                Standard Deviation of Y-Intercept =  0.34013
                Correlation Coefficient = -0.9919

                Standard Error of Estimate =   0.7392
                (measure of y-scatter about regression line)


                WRITE THESE RESULTS IN YOUR LAB NOTEBOOK !
        ***********************************************************************
```

Figure 15.4.10.2: The lsq Function. (CC-NC-BY-DUKE CHEM)

To perform a weighted linear least-squares analysis, you would use the command **wtlsq(x,y)**. This requires that you enter a weighting factor e.

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15.4.11: Last Line Editing and Recall

The arrow keys on the terminal can be used to edit mistyped commands or to recall previous command lines. For example, suppose you enter

```
log(sqt(atan(2*(3+4))))
```

You have misspelled sqrt. The response from Matlab is the error message,

Undefined function ‘sqt’ for input arguments of type 'double'.

Instead of retyping the entire line, simply hit the Up-Arrow key. The incorrect line will be displayed again and you can move the cursor over using the Left-Arrow key and insert the missing r.

```
log(sqrt(atan(2*(3+4))))
```

ans = 0.2026

The arrow keys on the keyboard work on copies of the previous input lines, which have been saved in a moderately sized input buffer. Here is a brief description of their function:

Last-line Editing and Recall Keys

Up Arrow Recalls previous lines.

Left Arrow Move left one character.

Right Arrow Move right one character.

Ctrl-U Cancel current line.

Ctrl-E Move to end of line.

Ctrl-A Toggle between insert and overtype mode.

Delete Delete character at cursor.

Backspace Delete character left of cursor.

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15.4.12: Saving Data

If you wish to save the variables in your workspace for later use, enter:

```
save filename
```

This saves all variables in the file *filename.mat*.. The next time you invoke Matlab, the workspace may be restored using:

```
load filename
```

We highly recommend that you save your data frequently as you work. This will prevent a major loss of data in the event of a system failure.

If you wish to save graphics, work from within the graphics window. Choose **Save** from the **File** menu. A dialog box opens up. Give your file a name, in the **File Name** box. You can select the file type from the **Files of Type** menu. Matlab graphics default to a .fig file type, and if you intend to open the graph again in Matlab that is a good option. If you want a picture of the graph for use in electronic lab notebooks (ELN's) or in your formal written reports you might prefer the .jpg format. The file will be stored in the specified directory (shown in the Save In menu) of your account associated with your NetID when you click on the **Save** button.

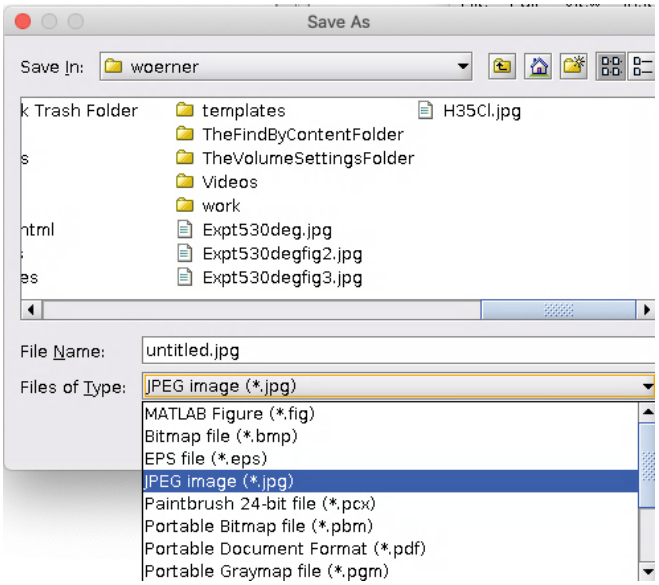


Figure 15.4.12.1: Saving a Figure.

Saved .fig files can be opened anytime, from the Matlab prompt, by typing

```
open filename.fig
```

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15.4.13: Deleting Matrices

If you wish to delete a variable from your workspace, enter:

```
clear name
```

where *name* is the name of the matrix or variable to be deleted.

> **Note**
>
> Be careful, because executing,
>
> **clear**
>
> by itself, clears **all** variables from the workspace!

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15.4.14: Quitting Matlab

Before you exit Matlab type,

```
diary off
```

if you had a diary running.

Exit Matlab by typing,

```
exit
```

Type,

```
exit
```

to close any xterm windows you have open. Finally, please remember to exit out of FastX if you are accessing Matlab through a FastX connection.

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15.4.15: Transferring Files Between Your Computer and Your Duke NetID Account

In several experiments this semester, you will use a lab computer for instrument control and data acquisition. There are times when it is convenient to have your raw data files uploaded to bohr so that you might analyze the data using Matlab. Additionally, there are times when files and figures (graphs) that are generated by matlab need to downloaded to your own computer. These operations can be done in the following manner.

1. To upload files from one of the lab computers to your online account:

1.1. Click on the 

icon found on the computer desktop to start the WinSCP file transfer program. The File protocol should be SFTP, and the port should be 22. Enter login.oit.duke.edu under Host Name. Enter your NetID (User name) and password, and click on Login. Click Continue at the Authentication Banner.

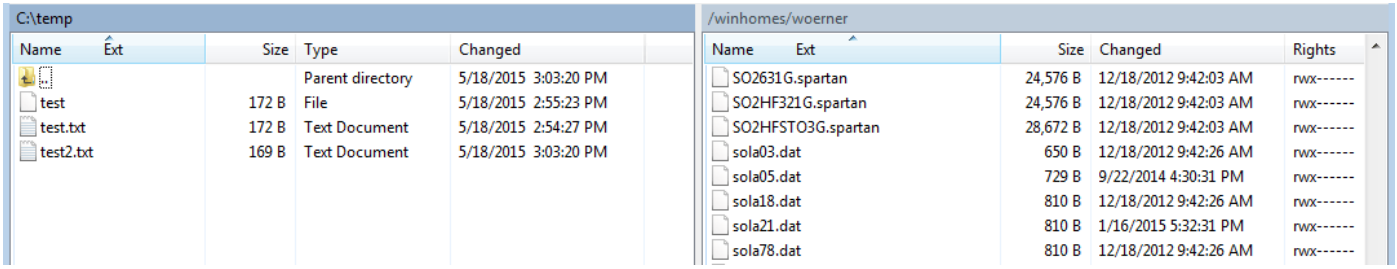
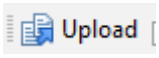


Figure 15.4.15.1: The Main WinSCP Window. (CC-NC-BY-DUKE CHEM)

1.2. You will see a dialog box, part of which is shown above. On the left-hand side of the screen is your local directory (i.e., the directory of the lab computer). It should default to the directory containing your data. If not, change the directory to the correct one. You should see a list of those files found in the local directory. On the right-hand side you will see the contents of your OIT account.

1.3. To transfer files from the local PC to your OIT account, first highlight the appropriate files you want transferred. Click on the 

button at the top of the screen. An Upload dialog box will appear. Click OK to copy your files from the local PC to your OIT account. Or, click on Transfer Settings if you want to check to see that the transfer is configured properly. (In general, the Transfer mode should be Text and the File modification should be No change.) Then click on **Copy**. Check to be sure all of your files are transferred and then exit your session by clicking the X at the upper right corner of the screen.

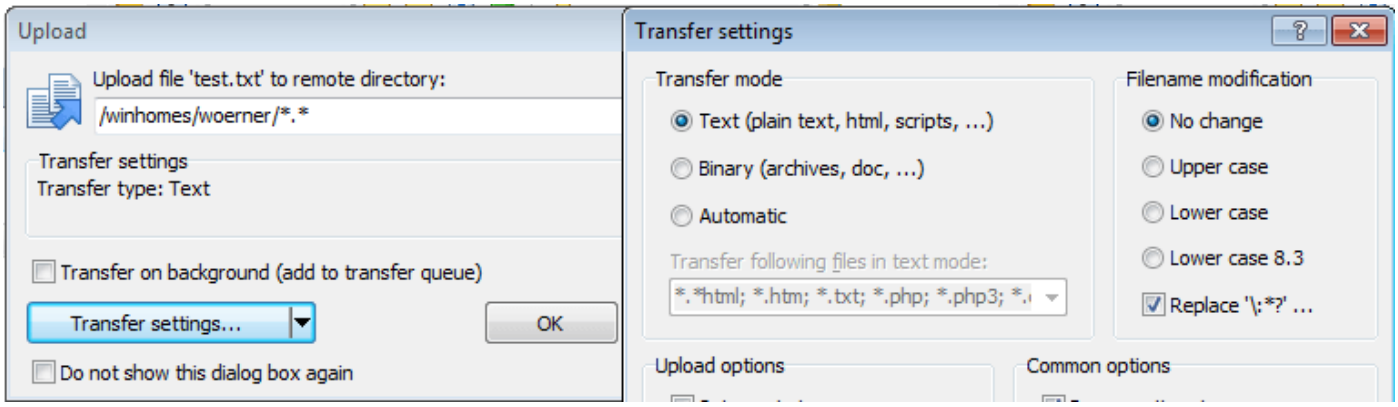


Figure 15.4.15.2: The WinSCP Upload Screen. (CC-NC-BY-DUKE CHEM)

2. **Downloading** files from your OIT account to your own **Windows** computer or to one of the lab computers is accomplished in the same manner, except that you should select the files you want to download, and execute the transfer from your OIT account to your local computer.

3. **Transferring** files back and forth between your **Macintosh** computer and your OIT account can be accomplished in the following manner.

3.1. From the Go menu (found when you are in your Finder), select **Connect to Server**.



Figure 15.4.15.3: The Macintosh Go Menu. (CC-NC-BY-DUKE CHEM)

3.2. In the text box at the next screen enter,

`smb://homedir.win.duke.edu/users/`*`the first letter of your NetID/your full NetID`*

An example of a correct server address is shown below, where w is the first letter of the NetID, and woerner is the NetID.

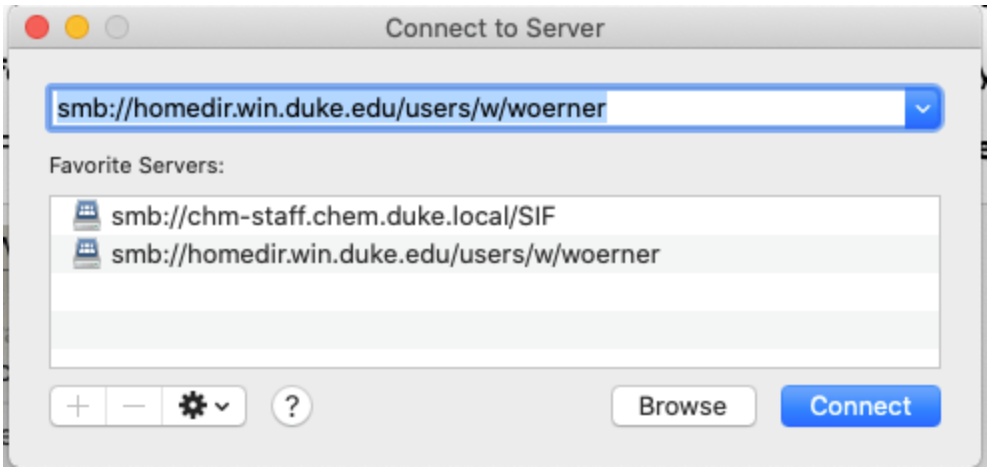


Figure 15.4.15.4: The Connect to Server Screen. (CC-NC-BY-DUKE CHEM)

3.3. Click the **Connect** button. You will be prompted for your NetID and Password.

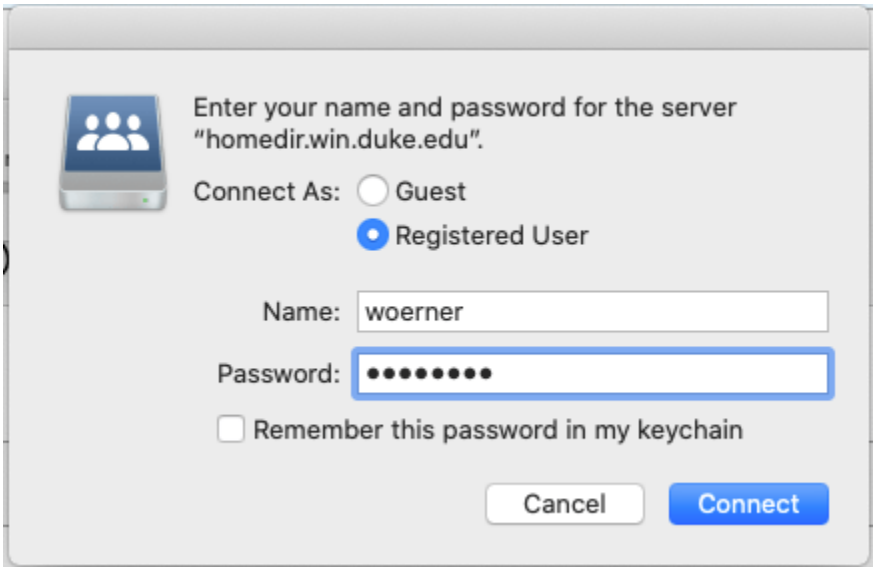


Figure 15.4.15.5: Login Screen. (CC-NC-BY-DUKE CHEM)

3.4. Once connected a new icon will appear on your desktop.



Figure 15.4.15.6: The Connectred Server Icon. (CC-NC-BY-DUKE CHEM)

If you do not see the icon appear, Check the **Finder Preferences**,

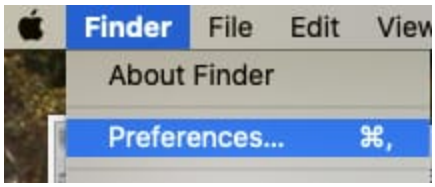


Figure 15.4.15.7: The Finder Menu. (CC-NC-BY-DUKE CHEM)

and make sure Connected Servers is checked.

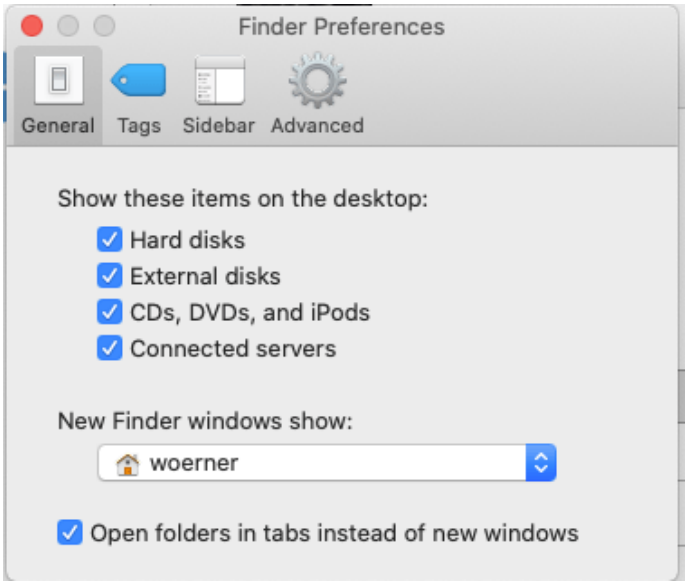


Figure 15.4.15.8: Finder Preferences. (CC-NC-BY-DUKE CHEM)

3.5. The connected server on your desktop acts like any other folder on your Mac. Click on it to open it and see the contents of your online OIT account. Drag and drop to move files back and forth between your Mac and your OIT account.

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15.5: TEMPORARY

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15.5.1: USING MATLAB (SUPPLEMENTAL)

> If you are a brand new Matlab user, or its been a long time since you've used it, the "hopw-to" sections of this manual may seem opaque. A great way to start it to run through the "Getting Started" tutorials from Matlab.

We will introduce you to using Matlab to perform numeric calculations. If you wish, you may save a copy of your work for printing later. This is done using the **diary** command, which captures a copy of all subsequent keyboard input and most of the resulting output (with the exception of graphs) to be written to a named file. If the file already exists, the output is appended to the end of the file. For example, the command,

```
diary exptA
```

will save your work in the file exptA. This file can be downloaded to your computer for later use as described in section 1.2.15. When you have completed your work, the command,

```
diary off
```

will suspend the diary.

> **IMPORTANT NOTE:**
>
> The diary command merely "records" your on-screen work. It does not save your data. Data must be saved as described in Section 1.2.12. Although diary files may be printed, they cannot be retrieved for viewing on the screen.

15.5.1.1: Entering Matricies

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15.5.1.1: Entering Matricies

Matlab works with essentially only one kind of object, a rectangular numerical matrix. In some situations, special meaning is attached to 1-by-1 matrices, which are scalars, and to matrices with only one row or column, which are vectors.

Matrices can be introduced into Matlab in several different ways. The easiest method for small matrices is to use an explicit list. The explicit list is surrounded by square brackets, and uses the semicolon, ; , to indicate the ends of the rows. For example, to enter a 3-by-3 matrix, we type:

```
A = [1 2 3; 4 5 6; 7 8 0]
```

This results in the output

A =

1 2 3
4 5 6
7 8 0

The matrix A is saved for later use. The individual elements in the input should be separated by commas or blanks and can be any Matlab expression. For example, typing

```
x = [-1.3, 4/5, 4*atan(1)]
```

uses Matlab like a calculator and results in

x =

-1.3000 0.8000 3.1416

Matrices entered, horizontally, as shown above, can sometimes be long enough to require more than one line. Matlab must be told when a wrap to another line is wanted. To do this, as you near the end of the line, add a space (spacebar) followed by three periods (...). Then hit enter. You will be allowed to continue entering numbers into the same matrix on the new line. Alternatively, if entering matrices horizontally is troublesome, you can always enter numbers vertically.

Typing:

```
y = [1
2
3
4
5]
```

results in:

y=

1

2

3

4

5

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15.5.1.2: Matrix Computation

We will run through some basic matrix operations. Operations and commands in Matlab are intended to be natural, in a matrix sense, not unlike how they might be indicated on paper. For example, our matrix A can be transposed with:

```
B = A'
```

which results in:

```
B =

1 4 7
2 5 8
3 6 0
```

Transposing x,

```
x = x'
```

results in:

```
x =

-1.3000
0.8000
3.1416
```

Matrix multiplication is indicated with:

```
C = A * B
```

producing:

```
C =

14 32 23
32 77 68
23 68 113
```

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15.5.1.3: Vectors

Vectors with regularly spaced elements may be generated using the colon:operator.

The statement

```
D = 1:4
```

results in

```
D =

1 2 3 4
```

Two colons may be used to create vectors with increments between the elements. Typing:

```
E = 0:0.1:0.5
```

results in

```
E =

0.0000 0.1000 0.2000 0.3000 0.4000 0.5000
```

Vectors are used often in Matlab because of the ease with which they allow data manipulation and function evaluation. When a function is applied to a vector in Matlab, the function is applied to each element of the vector. For example, consider taking the sine of the four elements in vector D above. Typing:

```
Y = sin(D)
```

results in

```
Y =

0.8415 0.9093 0.1411 –0.7568
```

A wide variety of data analysis functions are available that operate on vectors. Typical functions include cumulative sum,

```
cumsum(Y)
```

```
ans =

0.8415 1.7508 1.8919 1.1351
```

mean and standard deviation,

```
m = mean(Y), s = std(Y)
```

```
m =

0.2838

s =

0.7758
```

Other useful functions include:

max(x)	returns the largest element in the vector x
min(x)	returns the smallest element in the vector x
median(x)	returns the median value of the vector x
sort(x)	sorts the elements of x in ascending order
sum(x)	returns the sum of the elements of x

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15.5.1.4: Subscripting

Enclosing their subscripts in parentheses may reference individual matrix elements. The statement A(m,n) refers to the mth row, and nth column, of matrix A. For example, given a matrix A:

```
A =

1 2 3
4 5 6
7 8 9
```

the statement

```
A(3,3) = A(1,3) + A(2,2)
```

results in

```
A =

1 2 3
4 5 6
7 8 8
```

A subscript can be a vector. If X and V are vectors, then X(V) is [X(V(1)), X(V(2)), ..., X(V(n))]. For matrices, vector subscripts allow access to contiguous and noncontiguous submatrices. For example, suppose that A is a 10-by-10 matrix. Then,

```
A(1:5,3)
```

specifies the 5-by-1 submatrix, or column vector, that consists of the first five elements in the third column of A. Similarly,

```
A(1:5,7:10)
```

is the 5-by-4 submatrix of elements from the first five rows and the last four columns.

Using the colon by itself in place of a subscript denotes *all* of the corresponding row or column. For example,

```
A(:,3)
```

is the third column and

```
A(1:5,:)
```

is the first five rows.

In general, if v and w are vectors with integer components, then

```
A(v,w)
```

is the matrix obtained by taking the elements of A with row subscripts from v and column subscripts from w.

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15.5.1.5: Finding, Deleting, Adding or Replacing Data

The following examples will illustrate how to find, change, add or delete data in a vector. The same principles apply to manipulation of data in matrix form.

(a) Finding Data:

Suppose we wish to find the elements of vector V which are greater than or equal to 7:

```
V = [-2 3 7 -26 48 10 -8]', i = find(V>=7)
```

results in

V =

-2

3

7

-26

48

10

-8

i =

3

5

6

The statement, i = find(V>=7), returns a vector, i, containing the index of the elements of V which are greater than or equal to 7. The third, fifth and sixth elements of V are ≥ 7.

There are six relational operators that can be used in Matlab:

Relational Operators

< less than

<= less than or equal to

> greater than

>= greater than or equal to

== equal to

~= not equal to

(b) Deleting Data:

Specific elements in a matrix or vector can be deleted using the empty matrix (or vector), []. The statement

```
x = []
```

assigns a matrix of dimension zero-by-zero to x. To delete the elements of V which are greater than or equal to seven, use the command

```
V(i) = []
```

which returns

V =

-2

3

-26

-8

The elements of V which have indices given by the elements of i, are removed by assigning them to an empty matrix. Single elements may be removed in similar fashion. The command

```
V(3) = []
```

deletes the third element of V and returns

V =

-2

3

-8

An efficient way of removing rows and columns of a matrix is to assign them to an empty matrix. The command, **A(:,3)=[],** deletes column 3 of matrix A.

(c) Adding Data:

Suppose we wish to combine the elements of vectors V and U:

```
U = [3:2:10]', W = [V; U]
```

This returns

U =

3

5

7

9

W =

-2

3

-8

3

5

7

9

If we wish to add a single data point (-17) to the end of vector W:

```
W = [W; -17]
```

This returns

W =

-2

3

-8

3

5

7

9

-17

(d) Replacing Data:

To replace the fourth element of W with -12, enter the following

```
W(4) = -12
```

This returns

W =

-2

3

-8

-12

5

7

9

-17

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15.5.1.6: Output Format

The result of any Matlab assignment statement is displayed on the screen, as well as assigned to the specified variable or to **ans** if no variable name is given. The numeric display format can be controlled using the **format** command. **format** affects only how matrices are displayed, not how they are computed or saved (Matlab performs all computation in double precision).

If all the elements of a matrix are exact integers, the matrix is displayed in a format without any decimal points. For example,

```
x = [-1 0 1]
```

always results in

x =

-1 0 1

If at least one of the elements of a matrix is not an exact integer, there are several possible output formats. The default format, called the **short** format, shows approximately 5 significant decimal digits. The other formats show more significant digits or use scientific notation. As an example, suppose

```
x = [4/3 1.2345e-6]
```

The formats, and the resulting output for this vector, are:

format short

1.3333 0.0000

format short e

1.3333E+000 1.2345E-006

format long

1.33333333333333 0.00000123450000

format long e

1.333333333333333e+00 1.234500000000000e-06

For the long formats, the last significant digit may appear to be incorrect, but the output is actually an accurate decimal representation of the binary number stored in the computer.

With the short and long formats, if the largest element of a matrix is larger than 1000 or smaller than 0.001, a common scale factor is applied to the entire matrix when it is displayed. For example,

```
x = 1.e20*x
```

multiplies x by 1020 and results in the display

x =

1.0E+020 *

1.3333 0.0000

One final command, **format compact**, suppresses many of the line-feeds that appear between matrix displays and allows more information to be shown on the screen.

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15.5.1.7: The Help Facility

A HELP facility is available, providing online information on most Matlab topics. To get a list of HELP topics, type

```
help
```

To get HELP on a specific topic, type help **topic**. For example,

```
help eig
```

provides HELP information on the use of the eigenvalue function,

```
help []
```

tells how to use brackets to enter matrices, and

```
help help
```

is self-referential, but works just fine.

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15.5.1.8: ARRAY OPERATIONS

We use the term **array operations** to refer to element-by-element arithmetic operations, instead of the usual linear algebraic matrix operations denoted by the symbols * / \ ^ '. Preceding an operator with a period **.** indicates an array or element-by-element operation.

15.5.1.8.1: Array Addition and Subtraction

15.5.1.8.2: Array Multiplication and Division

15.5.1.8.3: Array Powers

15.5.1.8.4: Math Functions

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15.5.1.8.1: Array Addition and Subtraction

For addition and subtraction, the array operations and the matrix operations are the same, so + and - can be regarded as either matrix or array operations.

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15.5.1.8.2: Array Multiplication and Division

Array, or element-by-element, multiplication is denoted by **.***. If **A** and **B** have the same dimensions, then **A .* B** denotes the array whose elements are simply the products of the individual elements of **A** and **B**. For example, if

x = [1 2 3]; y = [4 5 6];

then,

```
z = x.*y
```

results in

z =

4 10 18

X = A./B is a solution to X.*B = A and X = A.\B is a solution to A.*X = B so, the expressions A./B and A.\B give the quotients of the individual elements.

```
z = x.\y
```

results in

z =

4.0000 2.5000 2.0000

To obtain the reciprocal of the elements of x, type

```
w = x.\1
```

This results in

w =

1.0000 0.5000 0.3333

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15.5.1.8.3: Array Powers

Element-by-element powers are denoted by **.^**. Here are several examples, using the above vectors x and y. Typing

```
z = x.^y
```

results in

z =

1 32 729

The exponent can be a scalar.

```
z = x.^2
```

z =

1 4 9

Or, the base can be a scalar.

```
z = 2 .^x
```

z =

2 4 8

Note

This last example illustrates one of Matlab's syntactic subtleties. Although it is difficult to see, the space between the digit 2 and the period **.** is important. If it were not there, the period would be interpreted as a decimal point associated with the 2. An alternative to the space is to use parentheses, forcing the correct precedence.

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15.5.1.8.4: Math Functions

Available math functions include the following:

MATH FUNCTIONS

Use the Help command to obtain further information on any of these functions

abs	absolute value or complex magnitude
sqrt	square root
real	real part
imag	imaginary part
round	round to nearest integer
exp	exponential base e
log	natural logarithm
log10	log base 10
sin	sine
cos	cosine
tan	tangent
asin	arcsine
acos	arccosine
atan	arctangent

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15.5.1.9: GRAPHICS

One of the major advantages of Matlab is its graphics capability. The graphics commands are natural and easy-to-use, yet still succinct, powerful, and extensible.

Scientific and engineering data are examined graphically in Matlab by using a "graph" command to create a plot on the screen. There are seven different types of "graph" from which to choose:

GRAPH

plot linear X-Y plot
loglog loglog X-Y plot
semilogx semi-log X-Y plot (x-axis logarithmic)
semilogy semi-log X-Y plot (y-axis logarithmic)
polar polar plot
mesh 3-dimensional mesh surface
contour contour plot

The **plot** command creates linear X-Y plots. Once the plot command is understood, logarithmic and polar plots are created by substituting the commands **loglog**, **semilogx**, **semilogy**, or **polar** for **plot**. All five commands are used the same way; they only affect how the axis is scaled and the data are displayed.

15.5.1.9.1: Basic Plots

15.5.1.9.2: Line Types

15.5.1.9.3: Multiple Plots

15.5.1.9.4: Manual Axis Scaling

15.5.1.9.5: Overlaying Plots

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15.5.1.9.1: Basic Plots

If Y is a vector, plot(Y) produces a linear plot of the elements of Y versus the index of the elements of Y. For example, suppose we would like to plot the numbers {0., .48, .84, 1., .91, .6, .14}. This is quickly accomplished by typing

```
Y = [0. .48 .84 1. .91 .6 .14];
plot(Y)
```

which results in a graph on the screen:

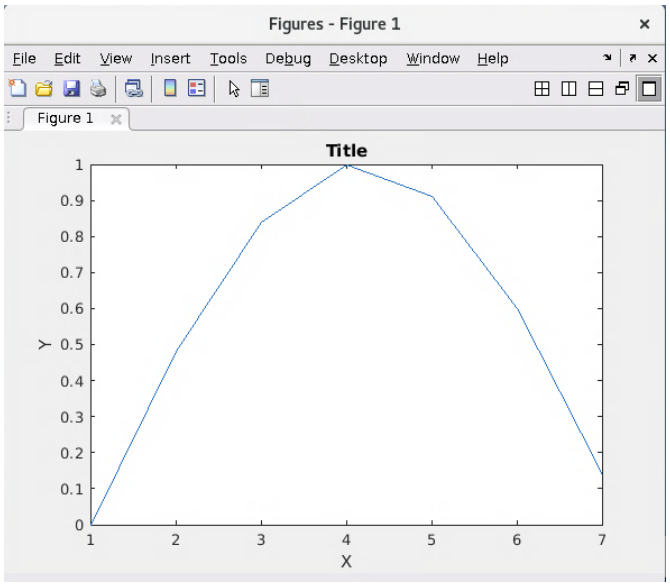


Figure 15.5.1.9.1.1: A Basic Plot. (CC-NC-BY-DUKE CHEM)

Notice that the data are auto-scaled and x- and y-axes are drawn. Use X Label; Y Label; and, Title from the Insert Menu to add a title and axes labels to your graph. Or, select Property Editor from the View menu. A Properties Editor box appears from which you can enter axes labels, a title and etc.

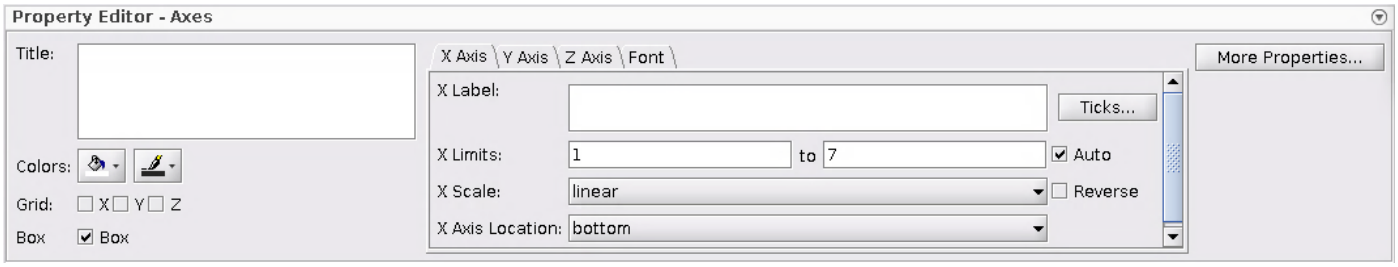


Figure 15.5.1.9.1.2: Property Editor. (CC-NC-BY-DUKE CHEM)

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15.5.1.9.2: Line Types

(b) Line types

The line types used on a graph may be controlled if the defaults are not satisfactory. Typically one does not connect data points with a line. Point plots using various symbols may be selected directly in the plot command. For example,

```
plot(X,Y,'x')
```

draws a point plot using x-mark symbols while

```
plot(X1,Y1,':',X2,Y2,'+')
```

uses a dotted line for the first curve and the plus symbol + for the second curve. Create vectors X1, Y1, X2 and Y2 and try this! Other line and point types are:

Line Type	Point Type
solid -	point .
dashed --	plus +
imag	imaginary part
dotted :	star *
dashdot -.	circle o
	x-mark x

Alternatively, the line type can be modified from within the Properties Editor window after the plot command is issued. Working with the graph above, with the Properties Editor window open, first select the arrow tool . Then click once somewhere on the actual data points. The data set will be highlighted and the Properties Editor window will change to display line properties. Under the Line menu select no line, and choose a marker from the Marker menu.

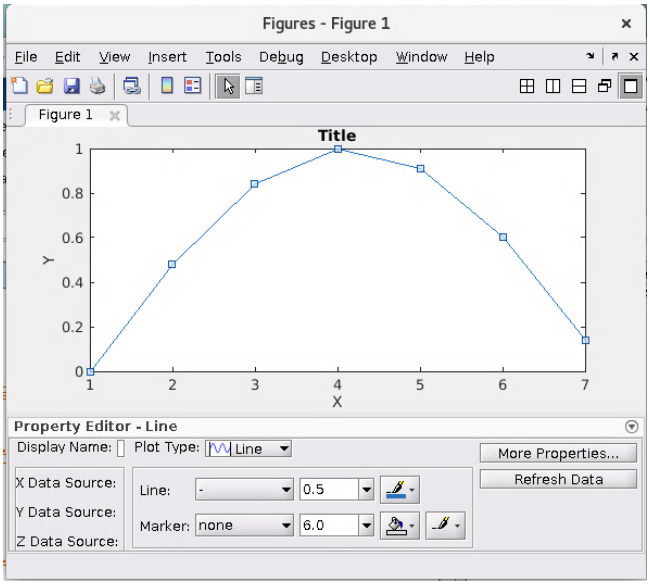


Figure 15.5.1.9.2.1: Line Editor.

Your graph will change accordingly. Finally, selecting More Properties from the Property Editor opens an additional options box.

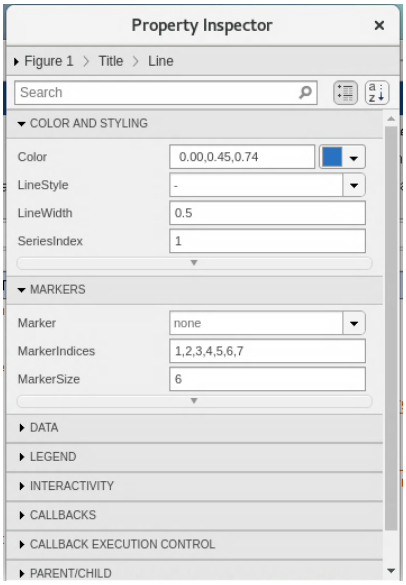


Figure 15.5.1.9.2.2: Property Inspector.

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15.5.1.9.3: Multiple Plots

The way to plot multiple lines on a single graph is to use plot with multiple arguments:

```
plot(X1,Y1,X2,Y2,...,Xn,Yn)
```

The variables X1,Y1, X2,Y2 etc. are pairs of vectors. Each x-y pair is graphed, generating multiple lines on the plot. Multiple arguments have the benefit of allowing vectors of differing lengths to be displayed on the same graph. Each pair uses a different linetype.

We can apply what we learned in the previous sections to plot simple functions. For example, to examine the behavior of the functions sin(x) and x2/100 on the interval from -15 to 15:

```
x = -15:.05:15;
y = sin(x);
z = x.^2/100;
plot(x,y,x,z)
```

which results in:

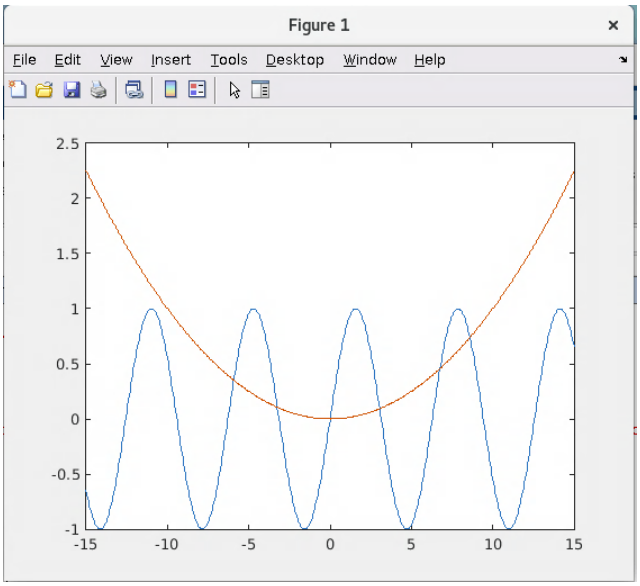


Figure 15.5.1.9.3.1: Multiple Plots.

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15.5.1.9.4: Manual Axis Scaling

In certain situations, it may be desirable to override the automatic axis scaling feature of the plot command and manually select the axis limits. Manual axis scaling is easily accomplished from the Properties Editor window mentioned above.

Alternatively, manual Axes Scaling can be accomplished from the Matlab workspace by creating a vector, V, with the following configuration

V=[X-min, X-max, Y-min, Y-max]

Working from the example graph above, let's say you wanted to scale the X axis from –5 to 5 and the Y axis from –1.5 to 1.5. Enter the following:

```
V = [-5, 5, -1.5, 1.5]
axis(V)
```

Retype the plot command plot(x,y,x,z) to observe the rescaled graph. The command **axis(V)** sets the axis scaling to the prescribed limits. If you reenter the command:

```
axis
```

autoscaling is resumed. Again, retype the command, plot(x,y,x,z), to observe the graph.

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15.5.1.9.5: Overlaying Plots

The command,

```
hold
```

holds the current graph on the screen. Subsequent plot commands will add to the graph, using the established axis limits and retaining the previously plotted curves. **hold** remains in effect until this command is issued again (i.e. the command **hold** can be "toggled" on and off).

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15.5.1.10: Linear Least Squares Analysis

To fit a straight line, y = mx + b, to a set of experimentally determined points

(x 1,y 1), (x 2,y 2), ..., (x n,y n) contained in the vectors [x] and [y], use **Basic Fitting** under the **Tools** menu in your graph window. Try this using the following data:

```
x = [-3.8 -1.2 0.75 3.1 5.6 8];
y = [8.2 6 3.3 1.6 -2 -6];
```

Selecting Basic Fitting from the Tools menu opens up an options box. Select **linear** as the fit type and choose how many significant figure you want in the calculation. A Linear Least-Squares line will be placed on the graph along with the equation for the line.

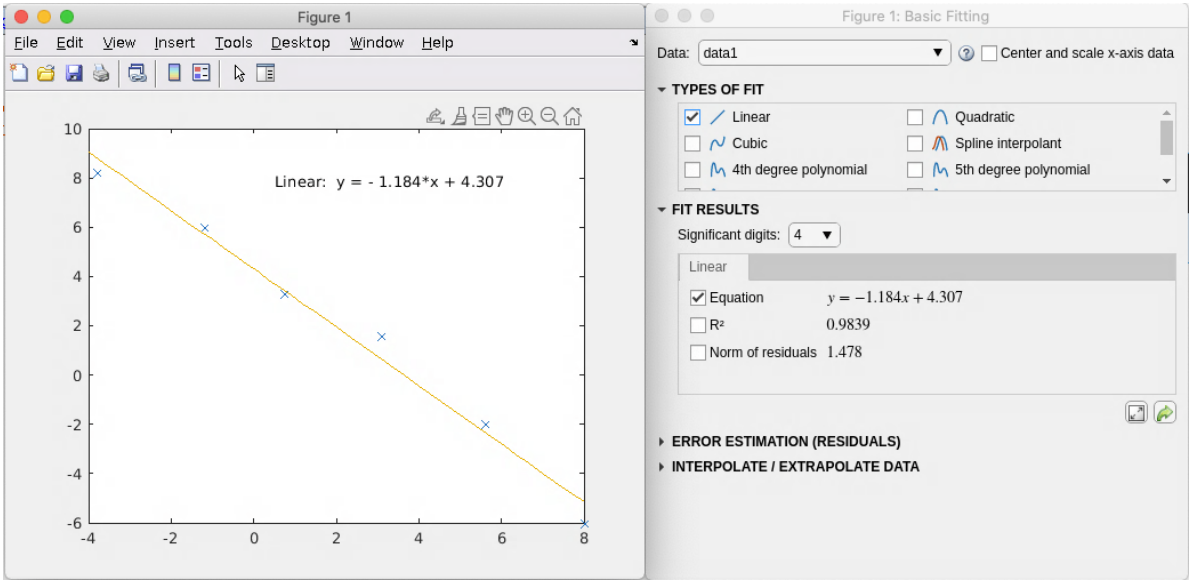


Figure 15.5.1.10.1: Basic Linear Fit. (CC-NC-BY-DUKE CHEM)

NOTE: Often for our purposes in the Physical Chemistry Laboratory it is often important to know the uncertainties (or standard deviation) in the calculated slope and intercept. To obtain calculated values of the slope, intercept, correlation coefficient along with the uncertainties in slope and intercept, use the **lsq** command. Using the current x,y data as an example, typing:

```
lsq(x,y)
```

returns the following:

```
>> x=[-3.8 -1.2 .75 3.1 5.6 8];
>> y=[8.2 6 3.3 1.6 -2 -6];
>> plot(x,y)
>> lsq(x,y)
        ***********************************************************************
                Slope =  -1.1839
                Y Intercept =   4.3066
                Standard Deviation of Slope = 0.075611
                Standard Deviation of Y-Intercept =  0.34013
                Correlation Coefficient = -0.9919

                Standard Error of Estimate =   0.7392
                (measure of y-scatter about regression line)


                WRITE THESE RESULTS IN YOUR LAB NOTEBOOK !
        ***********************************************************************
```

Figure 15.5.1.10.2: The lsq Function. (CC-NC-BY-DUKE CHEM)

To perform a weighted linear least-squares analysis, you would use the command **wtlsq(x,y)**. This requires that you enter a weighting factor e.

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15.5.1.11: Last Line Editing and Recall

The arrow keys on the terminal can be used to edit mistyped commands or to recall previous command lines. For example, suppose you enter

```
log(sqt(atan(2*(3+4))))
```

You have misspelled sqrt. The response from Matlab is the error message,

Undefined function ‘sqt’ for input arguments of type 'double'.

Instead of retyping the entire line, simply hit the Up-Arrow key. The incorrect line will be displayed again and you can move the cursor over using the Left-Arrow key and insert the missing r.

```
log(sqrt(atan(2*(3+4))))
```

ans = 0.2026

The arrow keys on the keyboard work on copies of the previous input lines, which have been saved in a moderately sized input buffer. Here is a brief description of their function:

Last-line Editing and Recall Keys

Up Arrow Recalls previous lines.

Left Arrow Move left one character.

Right Arrow Move right one character.

Ctrl-U Cancel current line.

Ctrl-E Move to end of line.

Ctrl-A Toggle between insert and overtype mode.

Delete Delete character at cursor.

Backspace Delete character left of cursor.

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15.5.1.12: Saving Data

If you wish to save the variables in your workspace for later use, enter:

```
save filename
```

This saves all variables in the file *filename.mat*.. The next time you invoke Matlab, the workspace may be restored using:

```
load filename
```

We highly recommend that you save your data frequently as you work. This will prevent a major loss of data in the event of a system failure.

If you wish to save graphics, work from within the graphics window. Choose **Save** from the **File** menu. A dialog box opens up. Give your file a name, in the **File Name** box. You can select the file type from the **Files of Type** menu. Matlab graphics default to a .fig file type, and if you intend to open the graph again in Matlab that is a good option. If you want a picture of the graph for use in electronic lab notebooks (ELN's) or in your formal written reports you might prefer the .jpg format. The file will be stored in the specified directory (shown in the Save In menu) of your account associated with your NetID when you click on the **Save** button.

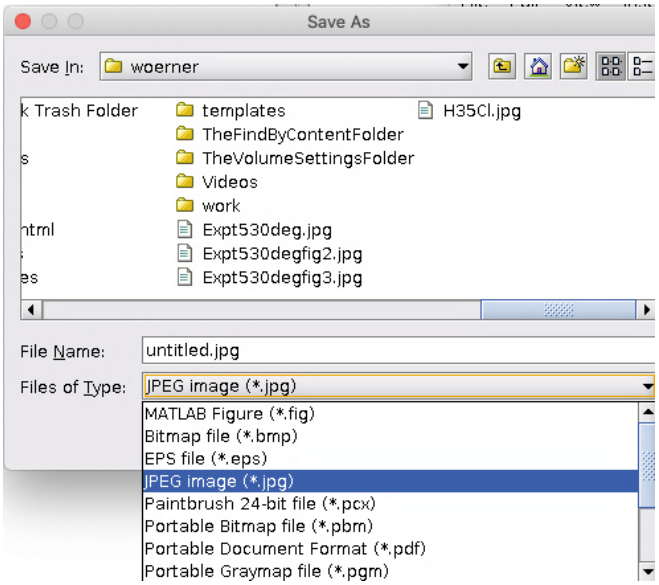


Figure 15.5.1.12.1: Saving a Figure.

Saved .fig files can be opened anytime, from the Matlab prompt, by typing

```
open filename.fig
```

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15.5.1.13: Deleting Matrices

If you wish to delete a variable from your workspace, enter:

```
clear name
```

where *name* is the name of the matrix or variable to be deleted.

> **Note**
>
> Be careful, because executing,
>
> **clear**
>
> by itself, clears **all** variables from the workspace!

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15.5.1.14: Quitting Matlab

Before you exit Matlab type,

```
diary off
```

if you had a diary running.

Exit Matlab by typing,

```
exit
```

Type,

```
exit
```

to close any xterm windows you have open. Finally, please remember to exit out of FastX if you are accessing Matlab through a FastX connection.

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15.5.2: Install Matlab on your own computer

Another way access MatLab is to download and install the software on your own computer. The MatLab software with the additional "toolboxes" will take approximately 4 GB of space on your computer. If you have enough space on your computer to operate this software you can find instructions for downloading and installing the software at the links below.

- Duke OIT's Software List: https://software.duke.edu/
- Duke MatLab Portal: https://www.mathworks.com/academia/tah-portal/duke-university-30359028.html

If the links above are not working, try to search "Duke MatLab" on an internet browser and you will find the most recent information. (And please inform your instructors of any dysfunctional links!)

Additional Installation Instructions

During the installation of the software, it will be most convenient if you select to also install the following toolboxes in the PRODUCTS screen of the MatLab Installer (See image below).

- Curve Fitting
- Statistics and Machine Learning
- Symbolic Math

If you forget to do this, it can be done later through the Apps Tab in MatLab.

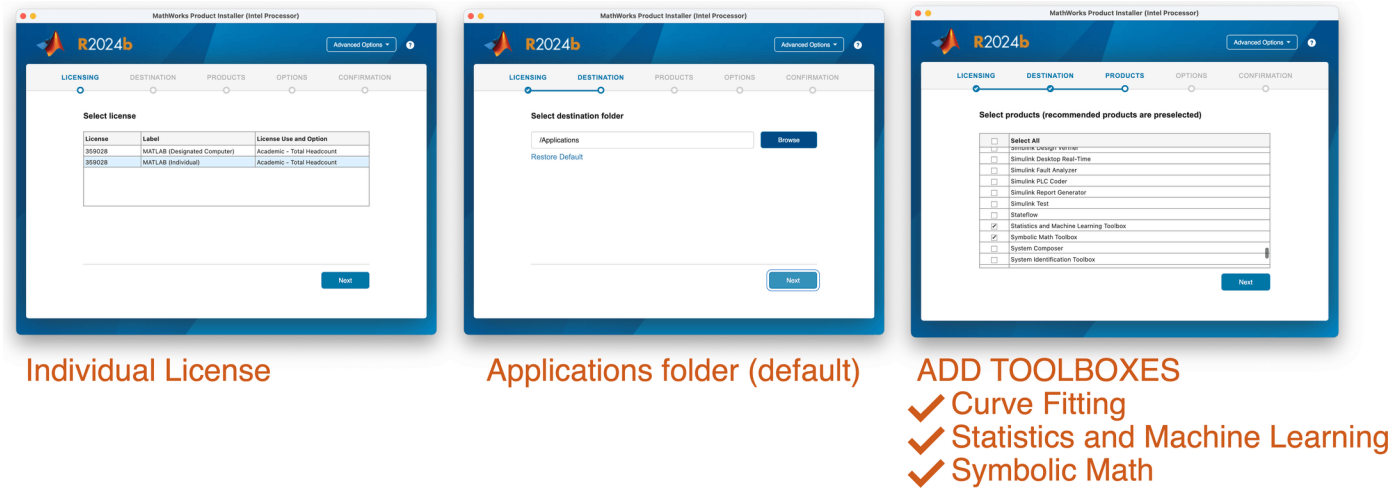


Figure 15.5.2.1: MatLab Install options. (Kathryn Haas; CC-NC-BY-SA)

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15.5.3: Invoking Matlab From the Lab Computers

INVOKING MATLAB FROM COMPUTERS IN THE LABS

1. To start Matlab on any of the computers in the lab:



FastX

1. Click on the FastX icon, on the main desktop screen, and then on the bohr.chem.duke.edu session. Enter your NetID and password and click OK. Once logged in, click on the + in the upper right of the bohr.chem.duke.edu window.

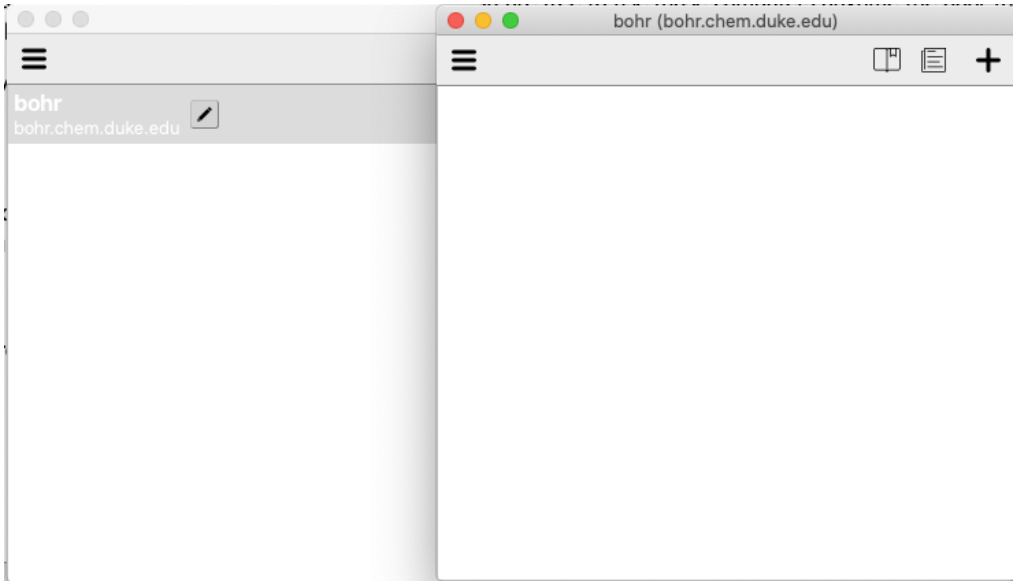


Figure 15.5.3.1: Connecting to Bohr through FastX. (CC-NC-BY-DUKE CHEM)

2. Click on one of the xterm choices from the new window that appears.



Figure 15.5.3.1: Choose xterm. (CC-NC-BY-DUKE CHEM)

3. An x-terminal window will open. At the prompt type,

```
matlab
```

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Overview

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