Laboratory Guidelines: CHEM 451 – Physical Chemistry

Fall 2022 Dr. Matthew Nee
Wednesdays, 12:40 – 5:10 pm OCH 3014

Overview: Physical chemistry, like all of the divisions of chemistry, is a living science. The theoretical principles it employs are derived from a variety of basic physical observations, and derived results can, in turn, be verified experimentally. In this laboratory, you will use a variety of analytical techniques to investigate the principles of thermodynamics, equilibrium, and kinetics. This lab will feel "different" from your other chemistry labs, in that there will be less emphasis on a product, more emphasis on measuring a phenomenon, and a lot of emphasis on error analysis and interpretation of data.

There will be six different report-based laboratory assignments for CHEM 451. For each laboratory, you will work in groups of two to three students, but you must write and submit your own laboratory report. Lab reports will be graded based on the presentation and analysis of data, as well as on the accuracy of the result. In each case, you will have two to three weeks to complete your lab report (see schedule on the last page of this document). Some opportunities for your work to be evaluated and improved prior to grading will be available.

Experiments: The experimental procedures for each lab will be available on Blackboard in advance of the scheduled date for performing the lab. A full tentative schedule is included at the end of this document. In some cases, more than one week may be necessary for a given lab. In such cases, some groups may work on the laboratory experiments, while others work on a different experiment or other activity. ***Even if you have no lab activity for a given week, you are responsible for attending lab lectures, unless otherwise announced.***

Other Activities: Throughout the semester we will meet to discuss various aspects of the course, including, but not limited to computer skills, peer evaluation, writing evaluation and improvement, and laboratory techniques and equipment. Given the current circumstances, if physical presence is not essential to the activities being done, they may be conducted electronically, by Zoom. I reserve the right to add activities during class time.

Safety: Students must wear appropriate clothing, protective goggles, and closed toe shoes at all times while in the lab room -- NO EXCEPTIONS! No food will be tolerated in the lab. Violations of safety regulations and contracts while in lab are grounds for dismissal from the lab and a zero on the assignment.

In the current semester, physical distancing will need to be maintained throughout the laboratory. This will be a challenge in some cases, as some labs will require simultaneous measurements to occur. Part of your planning for each lab will be to identify those possible challenges and to work with the additional protective equipment provided.

Lab Notebooks: Although we will not collect lab notebooks, we will look at them periodically during class. Points may be deducted from your lab report for inadequate or incomplete note-taking during the experiments. Your laboratory notebook is your only record of your thoughts and observations during the experiment. It is here that you should do the following:

- Before you begin work on an experiment (i.e., before you enter the laboratory), summarize the procedure to be followed in your notebook. Emphasize particular measurements, and make space to put measurements, so that you do not neglect an important measurement. ***This is a part of the pre-lab every week.***
- During the experiment, fill out these measurements, write down any observations, and include any possible sources of difficulty you encounter during the lab. Questions may occur to you, or you may have ideas about similar experiments that could be done. Write these down, and consider including them in your report.
- After the experiment but ***before you leave the lab***, check to be sure that you have collected all the data you need. It will be much easier to get a measurement now than it will be to repeat the whole experiment again later.
- You may choose to sketch out your calculations on another piece of paper, but you should definitely transfer those calculations to your notebook. Do not just write the result without any justification.

Although you may choose your type of notebook (you do not need to get one that produces carbon copies for this course), the one you choose should be bound (not wired, or with tear-out pages) and have at least a rigid cover. Composition books are a good, inexpensive choice. The best notebooks are hard backed, water proof, have numbered pages, and have graph lines instead of just horizontal ones, which is very helpful for plotting data. Never use pencil, and keep track of the date of your work, what experiment you are working on, and who is doing what in your group if you have chosen to divide up the labor. Don't forget to get all information from your coworkers as well!

Pre-lab assignments: Before each lab, you are responsible for reading and understanding the laboratory procedures, and for having laid out the basics of the calculations that will be necessary for the report. Note that for every lab, part of the pre-lab expectations will be to prepare your notebook with a concise summary of the experimental procedures, and you may find it helpful to make a list of data that needs to be collected in advance.

Formal Written Reports: One of the most important parts of lab is communicating what you have done. After all, if you make a great discovery, but cannot explain to anyone what you have done, you may as well have done nothing. Four of the six labs will require formal, typed reports following the format described at the end of this document. Two labs (Bomb Calorimetry and Impact of Ionic Strength) will have lower-value, less formal reports. Even for formal reports, calculations may be submitted handwritten, but should be referenced as an appendix in the discussion section of your report. **Everyone must submit a draft for the first lab.** At least two weeks have been allotted to complete your report so that you will have time to submit a draft with enough time for me to comment on it and return it to you for revision. Revisions will be most effective (and easier) if your draft is effectively complete when submitted.

Laboratory reports will be graded according to the grading rubric attached. **All lab reports (formal and informal) must be typed, 1.5 spaced, 11-point font with ¾" margins on all sides.** These are not necessarily the defaults for Microsoft Word, so you may need to change them. The font you choose should be professional and readable. Although Times New Roman tends to be the default font, others use Garamond, Palatino, or Bookman for their wider characters. The marking process will include grammar, spelling, punctuation and usage. Although these characteristics are not the primary objective of the lab report, they are an important aspect of writing; significant or numerous errors will result in a loss of up to 10 points for a given report.

All formal reports should contain the sections similar to a journal article in physical chemistry:

1. ***Introduction*** (1-1.5 pages) – Summarize the background and motivation for the experiments. Why is it important and interesting to collect and analyze these data? What are the important theories and concepts related to this material? Remember, do not simply paraphrase the lab manual, which has a different purpose than your introduction. Write in your own words what the reader needs to know in order to understand what you have done in the lab and why. References should be cited as appropriate. ***Include all equations*** that you will use in your calculations (numbered, as in a journal article or a textbook), so that you can refer to them later in your discussion section. If you do not use an equation later, there is no need to number it. In fact, you should seriously consider deleting it entirely unless it makes a major contribution to the reader's understanding.

2. ***Experimental (or Computational, or both) Methods*** (usually only ½ page or so) You should incorporate **in narrative** the procedure performed and the measurements taken. Be concise but complete. It is not acceptable to copy the numerical list of directions from the lab manual, in part because in a report, you are describing your experiment, not giving instructions. All non-standard laboratory equipment being used should have a complete description, and figures to explain it as necessary. Record detailed measurements that are important to getting correct results, but this is surprisingly rare. More often, you should prefer language like "5 g of carbon dioxide solid were added to the container", rather than "5.145 g….", with the detailed measurements included in your results section as appropriate. You should write your experiment and results sections in the past tense, since they are a record of what ***was done (in past tense, passive voice, third person)***.

3. ***Results and Discussion*** (2 to 4 pages) – Present your data in a table (where appropriate: if you are comparing two or more different experiments in which the same measurements are made) and in narrative form. Describe trends seen, and any deviations from those trends. For each type of calculation that you will perform, describe the data first, including the errors in the measurement, then describe the calculation process, then error propagation, and finally comparison to literature or theoretical values. For each measurement, discuss anything that happened during the experiment which could have an effect on the results. Units and numerical estimates of errors (an indication of the reliability of your measurements) must be included for all data. These describe the precision of your measurement, so they belong with the measurements themselves, and will then be used to propagate in your calculations. For the discussion part (not a separate section), interpret your data. This is the most important part! Use figures with captions, and discuss how any calculations were done. Your complete calculations should be in an appendix, but you must refer to the equations used and to the appendix itself:

> "Each value for γ was calculated using Eq. 2, as shown in the appendix. The results of these calculations are summarized in Table 3."

Any figure or table must have both a number and a descriptive caption. Even though it seems redundant, the content of all figures and tables must also be referenced and described in the narrative. As an example of the usage of figure, table, and equation references, consider the following:

> "The natural logarithms of the temperature-dependent rate constant data are plotted as a function of inverse temperature in Fig. 2. Each temperature is assigned a different color for ease of comparison. Using the Arrhenius Equation (Eq. 3), we calculate the activation energy of the reaction without catalyst to be 1.7×10^{-4}, and 2.8×10^{6} upon the addition of catalyst. These data, including a comparison with literature data,[4] are tabulated in Table 5."

In this case, we describe the contents of a figure to put it into context. Then, we reference the relevant equation (Eq. 3) that we used in calculating the desired information (the activation energy). Then, for ease of finding results, we tabulate the data (Table 5) to compare it to literature values, and we include a reference ([4]) to the source of those data. The reference will be noted at the end of the document. This statement would, of course, be followed by a thorough evaluation of the errors: are the experimental data within error bars of the literature values? How were error bars calculated? What were the major sources of error? Would each source of error increase or decrease the value of your result? Why? **Clearly answer any questions posed in the lab manual (not just those posed at the end!) in narrative form.**

4. ***Conclusions*** (½ to 1 page) – A conclusion is not the same as a summary, but the conclusions section should begin with a summary of the final numerical results. It is not helpful to summarize all the data, only the final result. Include error bars. What conclusions can you draw from your new data? Did you obtain or observe what was predicted? Extend what you summarized in the Results and Discussion section to connect to the big picture ideas in the introduction. Discuss how your data might be useful to others, or what further experiments might help clarify your results. If there is an accepted literature value for your experiment, state this and compare your results to this standard. In other words, what was the accuracy of your final result? What improvements could be made? Would they improve accuracy, or precision? What broader conclusions can you draw from your experiment and its results? What experiments might further enlighten the questions at hand?

5. ***Safety*** – The safety and health hazards for any compounds used in the experiment should be cited as well. After this citation, summarize the safety and health hazards in one or two sentences. Cite references such as MSDS or other descriptions of the experiment (for example, from the *Journal of Chemical Education*).

6. ***References*** – All should follow a normal scientific format, such as the following book reference for a popular physical chemistry text:

> McQuarrie, D. A.; Simon, J. D. *Physical Chemistry: A Molecular Approach*, 2nd Edition; University Science Books: Sausalito, 2009; pp. 457-493.

For a journal article, the volume, the first page and year are always included, the title of the article is in quotation marks, and the abbreviated title of the journal (these are standardized) appears in italics (like the book title above):

Nee, M. J.; Osterwalder, A.; Zhou, J. and Neumark, D. M., "Slow electron velocity-map imaging of the methoxide anion", *J. Chem. Phys.* **125**, 014306 (2006).

Cite the original source of any data wherever possible. The CRC, Merck index, and other data sources *are* acceptable as references, as are journal articles and books, including your text. Web citations generally are not acceptable except for MSDS. For examples of citations of various references (including MSDS and electronic sources), use the ACS styleguide. The University of Wisconsin kindly provides examples on its website:

http://chemistry.library.wisc.edu/writing/acs-style-guidelines.html

For an MSDS:

Argon; MSDS No. 00104; Airgas: Radnor, PA, September 20, 2021. http://www.airgas.com/documents/pdf/001004.pdf (accessed 9/20/11).

For other data from a database:

National Library of Medicine. Environmental Health and Toxicology: Specialized Information Services. http://sis.nlm.nih.gov/enviro.html (accessed Aug 23, 2021).

It is ***not*** okay to cite Wikipedia or other unreviewed sources. Even so, a well-written Wikipedia article will include references to established references on the subject in question. In that case, you should cite the original source only after you have verified its appropriateness.

Presenting Data in Graphical and Tabular Form: You have no doubt heard that "a picture is worth a thousand words." So, too, a graph is worth a thousand data points (sometimes more!). Graphs of data allow us to develop an intuitive understanding of the underlying pattern of the data, and often aid tremendously in interpretation. In most labs, you will have data that will be best presented in the form of a graph. Although you are welcome to use the spreadsheet of your choice, I will only be able to help you directly with MS Excel, which is available at all computer labs.

A few guidelines should be kept in mind when you are presenting your data in a lab report:

1. Always include axes and units.
2. Make lines and points large enough to see clearly, but not so large that it is difficult to see where things are.
3. Avoid background colors and lines.
4. Include a legend on the graph if there is more than one series, but not if only one dataset is plotted.
5. Include a descriptive caption ***beneath your figure*** that explains in words what the graph or diagram shows, as in the following example on the next page.
6. Tables should be readable, with text centered in the column. The MS Word table function should be used to generate tables. An example is given below. Note that both units and uncertainties are given in the column heading, and that, unlike for figures, captions for tables

are placed ***above the table***. Note that, because the table would be split across pages, I have had to place it (whole!) on the next page, rather than here.

7. Refer to all tables and figures in the text by their number:

    "Table 1 contains the data before and immediately after adiabatic expansion, as well as the pressure following thermal equilibration."

8. Size tables and figures to be either the full width of the margin (7"), or half-width (3.5"). If they are half width (which is the most common), wrap the text around the figure as in the example on the next page.

An example of a page in a lab report with a figure and a table might appear as shown below:

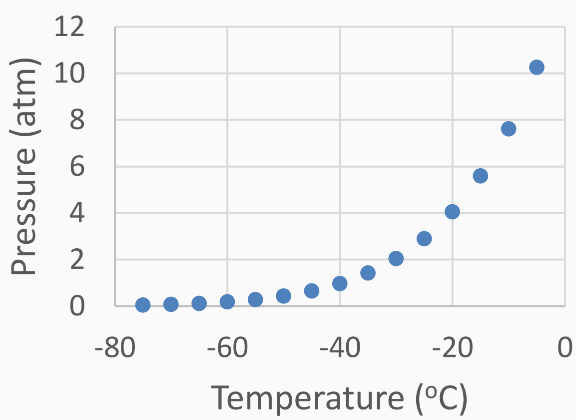

Figure 1. A plot of water pressure as a function of temperature along the solid/vapor equilibrium line. Pressure was measured as temperature increased. The triple point is observed at a pressure of 12 atm at 0°C.

Text text text text text text text. Text text text text text text text.

Table 1. Data from the adiabatic expansion experiment, with pressures before expansion (P_1), immediately following expansion (P_2), and after thermal equilibrium (P_3).

Gas	P_1 (torr ± 10 torr)	P_2 (torr ± 10 torr)	P_3 (torr ± 10 torr)	Temp. Drop (K ± 8K)	γ (±0.4)
Ar	874	790	821	11.9	1.60
N_2	882	790	813	8.5	1.35

Calculating and propagating errors: In everyday language, error means something wrong. However, in scientific contexts, it refers to the experimental uncertainty in a measurement. No measurement is 100% certain, and all numbers must include an error associated with them. For a raw data point, the error often comes from the instrumental precision, which is usually listed on the instrument itself. Other times, the experimenter must make a reasonable estimate of the error. In either case, all errors need to be explained:

> All temperature measurements had an uncertainty of ±0.1 K because the thermometer was marked to 0.1°C. Pressures were estimated to be ±0.02 atm based on fluctuations occurring during measurement.

When calculations are performed, the experimental errors must be propagated through the calculation. Strictly speaking, errors should be propagated using a method which involves partial derivatives with respect to every variable involved. We will introduce this idea for some labs, but often a quick estimate is just as appropriate. Unless otherwise noted, we will use a "worst case scenario" type of calculation. Here, the calculated result is determined first without considering the error. Then, the result is calculated again, this time adding or subtracting the uncertainty to the measurement, such that the largest deviation is observed. The difference between these two measurements is the uncertainty in the final result. An example is shown below:

$$\Delta_{vap}\bar{H} = R\left(\frac{T_1T_2}{T_2-T_1}\right)\ln\left(\frac{P_2}{P_1}\right) \qquad \begin{array}{ll} T_1 = 271.0 \pm 0.2K & P_1 = 0.91 \pm 0.03\,atm \\ T_2 = 281.0 \pm 0.2K & P_2 = 0.98 \pm 0.03\,atm \end{array}$$

Here, the first step is to insert the values for T_1, T_2, P_1, and P_2 into the formula and solve for $\Delta_{vap}H$. Note that R is a fundamental constant, so there is not an uncertainty associated with it:

$$\Delta_{vap}\bar{H} = 8.314\frac{J}{mol\,K}\left(\frac{(271.0K)(281.0K)}{281.0K-271.0K}\right)\ln\left(\frac{0.98\,atm}{0.91\,atm}\right) = 4692\frac{J}{mol} = 4.7\frac{kJ}{mol}$$

All terms have units associated with them. In the end, the value should have no more than 2 significant figures because the pressure terms have only 2 significant figures. Now, we must decide which values to use to derive our worst-case value. We will seek the largest value of $\Delta_{vap}H$ we can obtain. For the pressures, this is straightforward: we use the maximum value for P_2 (0.98 + 0.03 = 1.01 atm) and the minimum value for P_1 (0.91 – 0.03 = 0.88 atm). This will give the largest value of for the $\ln(P_2/P_1)$ term.

Temperature is a little trickier. Both temperatures appear twice in the calculation, and ***we must use the same value each time a variable appears***. As it turns out, the largest value for the temperature term arises from taking the maximum value in T_1 and the minimum value in T_2. Thus, the final calculation yields:

$$\Delta_{vap}\bar{H} = 8.314\frac{J}{mol\,K}\left(\frac{(271.2K)(280.8K)}{280.8K-271.2K}\right)\ln\left(\frac{1.01\,atm}{0.88\,atm}\right) = 9087\frac{J}{mol} = 9.1\frac{kJ}{mol}$$

We see that our estimate for the uncertainty in $\Delta_{vap}H$ is (9.1kJ/mol) – (4.7 kJ/mol) = 4.4 kJ/mol. Thus, we report our result as 4.7±4.4kJ/mol.

Academic Dishonesty: Physical Chemistry lab reports should be treated as models for reporting research data. As such, the University's policies on academic dishonesty, very clearly outlined in the *Undergraduate Catalog*, will be applied in this course:

"Following the procedures of due process, if the WKU Code of Student Conduct is violated, the responsible parties will go through the University's disciplinary process, which is intended to be a fair and educational experience. Any WKU student may be expelled, suspended, placed on probation or given a lesser sanction for one or more of the following causes: Dishonesty, such as cheating, plagiarism, misrepresenting of oneself or and organization, or knowingly furnishing false information to the University…"

Plagiarism includes, but is not necessarily limited to, the following offenses:

1. Copy, ***in whole or in part, including sentences or sentence fragments***, of a published work. The term "published work" also includes documents available electronically through websites or other means. "Copying" includes ***paraphrasing***, which is the restatement of sentences or paragraph in different words. Such offenses could range from a warning or request to rewrite the assignment with a penalty assessed, for a first offense, to zero credit for the sections copied, to a zero on the entire assignment for work copied to a significant extent. Multiple offenses are likely to result in a grade of F being given for the course, and report for student disciplinary action as outlined in the *Catalog*.

2. Direct copy, ***in whole or in part, including paraphrasing***, of work between students. It is typically not possible to distinguish the original from the copy. Thus, in a case of plagiarized work between students, both students will receive deductions. Consequences for such offenses are equivalent to those for copying of published material.

A warning for either type of offense serves as a warning for all types of academic dishonesty violations, and similarly for penalties.

Grading: Grades are assigned separately for CHEM 450 and 451. The formal laboratory reports (combined) will be worth 60% of your grade, meaning each is worth 15% of the grade. 20% of the grade will come from informal reports (a total of two, each worth 10%), and 20% will come from participation, which will be evaluated liberally. Good attendance and attitude, willingness to participate as a team member, readiness for lab, and attention to safety will earn full participation points. The breakdown within a formal lab is summarized in the grading sheet on page 10 of this document.

Review this checklist before your submit each lab report to be sure you have done everything!

General:

- ☐ Name, date, lab partners, page numbers
- ☐ All sections are there, including appendix
- ☐ **Writing has been proofread, edited, and proofed again**

Intro and Experiment:

- ☐ Context for the experiment (including objective statement for the lab) is clearly identified
- ☐ All equations used later are numbered, connected logically to text, symbols explained.
- ☐ Knowledge is described in present tense.
- ☐ Experiment is described, including a diagram as appropriate, using past tense, passive voice, third person

Results and Discussion:

- ☐ Data table(s) has descriptive caption above, or figure has descriptive caption below, and is referred to by name/number (e.g., Table 1) during the description in the narrative
- ☐ Data and calculations are described in narrative, including how the uncertainties were determined for each type of measurement
- ☐ All values have uncertainties and units listed
- ☐ Each calculation has a narrative in discussion section that refers to the equation used and to the appendix for calculations (only one example of each calculation is needed)
- ☐ Final results have error bars, and the method used to calculate them is noted briefly, including any assumptions about experimental uncertainties that were neglected
- ☐ Clear, concise statement is made on whether literature/theoretical values are within error bars of experimental values, and the implications of this for assessing experimental accuracy and precision
- ☐ Error sources suggested are consistent with the direction and magnitude of the numerical error
- ☐ All lab handout questions are answered

Conclusions:

- ☐ Results are restated, including error bars
- ☐ Single largest error (or maybe two if they are nearly the same) are clearly identified, and a means of improving the experiment by reducing that error is given
- ☐ If propagated errors do not account for discrepancy between experiment and literature/theory, additional possible errors must be discussed
- ☐ Big picture impact: Is this a good method of measuring the desired quantity? What extensions of this information can you identify?

Safety/References:

- ☐ Major hazards are identified, MSDS referenced, as well as references for background and literature values
- ☐ Numbered references are cited throughout the document, numbered in the order in which they are first cited in the text

Chemistry 451 Lab Report Grading Sheet

Name:______________________________ **Lab Partners:**______________________________

Experiment: _________________________ ______________________________

Introduction: 15 points

____/3 Name, title, date, lab partners names, grading sheet are included and correct.

____/2 Clear statement of the objective of the experiment is presented.

____/10 most important ideas and equations (define all symbols!) for the lab are concisely summarized.

Methods: 10 points

____/5 Instrumental apparatus is explained and diagramed as necessary.

____/5 Experimental description allows another 451 student to reproduce your work.

Results and Discussion: 50 points

____/15 All data is clearly presented in a table or graph that is referenced and described in the text.

____/5 All data has units and experimental uncertainty clearly identified.

____/10 Calculations and derived information are discussed briefly in narrative, and appendices referenced.

____/10 Final results and all additional information requested in handout is presented clearly in narrative.

____/5 Literature/ theoretical values are listed; appropriate comparisons are made, including error propagation.

____/5 Major sources of error given (includes magnitude and direction that they would impact final result).

Conclusions: 10 points

____/4 Quantitative summary of results (and uncertainty) reflects the objective statement from the introduction.

____/4 Discussion of errors suggests ways to improve or fatal flaws (goes beyond what is in the discussion).

____/2 Results are placed into the context of the broader scientific picture, with future applications noted.

Safety/References: 5 points

____/3 Major safety issues are addressed, MSDS are cited.

____/2 Citations for introduction, safety and literature or theoretical values are correct and complete.

General Writing: 10 points

____/5 Scientific writing style is used, including proper tenses and voices.

____/5 Organization, sentence structure, and flow make the report easy to follow and understand.

______/100 Total Score

CHEM 451 Tentative Lab Schedule: Spring 2022

Week	Date	Lecture	Activity	Outcome
1	8/24	Lab Safety and Reports	Data Analysis and Lab Reports	Ready for semester
2	8/31	Propagating Error	**Lab 1: Adiabatic Expansion**	**Draft Report: 9/9** **Final Report: 9/23**
3	9/7	Structuring Formal Reports	Scientific Writing Shortcuts	
4	9/14	Calorimetry Calculations	**Lab 2: Bomb Calorimetry**	**Informal Report: 9/28**
5	9/21	Lab Catchup and Discussion	Exam discussion	Ready for Lab 1 Report
6	9/28	Temperature and pressure measurements in lab	**Lab 3: Phase Diagram of CO_2**	**Report: 10/14**
7	10/5	Lab 3 data workup discussion	Good plots for Lab 3	Include in Lab 3 Report
8	10/12	Temperature-Composition phase diagrams	**Lab 4: Binary Phase mixture**	**Report: 10/28**
9	10/19	Getting “good” data	Plots for Lab 4	Include in Lab 4 Report
10	10/26	Effects of ionic strength	**Lab 5: Equilibrium and Ionic Strength**	**Informal Report: 11/16**
11	11/2	Equilibrium Lab Calculations	Lab 5 calculations primed	Include in Lab 5 Report
12	11/9	Measuring kinetics with spectroscopy	**Lab 6: Kinetics of Crystal Violet**	**Report: Monday 11/28**
13	11/16	Kinetic Data Analysis and Searching the Literature	Ready to Finish Lab 6	Include in Lab 6 Report
14	11/23	Thanksgiving Break – No Lab		
15	11/30	Numerical Methods in Kinetics: Optional	**Lab 7: Computational Kinetics Workshop**	Worksheet due 5/2, worth up to 20 Extra Credit Points