Pchem 'Cloud' Project 1 - The Properties of Gases

ASU Online CHM343 – Spring 2023

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OBJECTIVE: Elementary physical chemistry (BCH 341 or CHM 341) starts with the introduction of gas properties with an emphasis on molecular concepts and thermochemistry. Project 1 in online physical chemistry laboratory (CHM 343) aims to complement lecture material (e.g., Focus 1 from 'Elements of Physical Chemistry'[1]) through a combined (i) computational, (ii) experimental and (iii) data science (data and error analysis) project. In this online physical chemistry (Pchem) lab project, students are asked to use computational (electronic structure calculations) and experimental (acoustic interferometry) techniques to acquire data that allows for a determination of the heat capacity ratio (and diffusivity) of one or more common gases (e.g., He, N_2, CO_2 and Ar) or gas mixtures (e.g., air). An unknown gas will also be provided as part of the remote acoustic interferometer setup and students should be able to use their experience with measurements on known gases to determine the heat capacity ratio and identity of this unknown gas. An emphasis is placed on both acquiring the computational and experimental data, as well as the data analysis required to make the relationship to molecular theory. A further requirement of physical chemistry is quantitative error analysis and the proper propagation of error through multi-step data analysis and calculations (supplemental information). Students will be evaluated through their project report, and peer review evaluations.

INTRODUCTION

Of the three states of common molecular aggregation, only the gaseous state allows a comparatively simple quantitative description. Hence, the reason it is often emphasize in physical chemistry.[1,2,3] The aim of much of physical chemistry is to interpret quantitatively the observed properties of macroscopic systems in terms of the kinds and arrangements of atoms or molecules that make up these systems. Structurally, gases are nature's simplest substances; a simple model and elementary calculation yields results in good agreement with experiment. The kinetic theory of gases provides a beautiful and important illustration of the relation of theory to experiment, as well as of the techniques that are commonly used in relating structure to properties.[4]

Two common physical chemistry laboratory exercises for exploring the properties of gases are the determination of the ratio of the heat capacity of a gas at constant pressure to that at constant volume (C_P/C_V) and the determination of the diffusivity of a gas or gas mixture.[5] Often several gases are studied, and the results are analyzed and interpreted in terms of molecular theory (e.g., molecular degrees of freedom). The background material for both the heat-capacity ratios of gases and the diffusion of gases is covered extensively in the optional textbook for CHM 343, 'Experiments in Physical Chemistry'[2] and the CHM 341 textbook, as well as numerous sources online (Wikipedia is an excellent resource for all background material associated with this project).

The design of online CHM 343 projects has three major components: (1) Computational, simulations, estimations and/or predictions; (2) Chemical and biochemical molecular experiments and data collection; and (3) Data and Error Analysis with an emphasis on the relationship between theory and experiment or computational 'experiments'. The goal is to use all three components to develop an in-depth understanding of each project. Each of these components can be done as a remote 'online' student. The computational, data analysis, error analysis, data science and project reports are all easy to complete with standard online tools. The direct lab experiments are definitely the challenging component to bring a 'hands-on' lab experience to online/remote students that is on-par with in-person laboratories. That is ultimately the long-term goal of ASU-Sync and ASU-online, which we are working to use and build new technologies to best facilitate. For the experimental determination of the ratio of the heat capacities of gases, we will have ASU 'Cloud' (Remote) labs as well as an optional DIY 'home' lab.

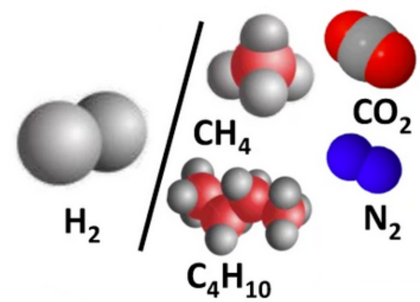

Figure 1 - Space filling model for several common molecular gases.

The goal of CHM 343 is to reinforce physical chemistry concepts through experiment. This includes both laboratory and computational 'experiments'. It is often the case that a student is partial to direct (hands-on) lab experiments or the more visualization of computational experiments. These projects are designed to be flexible and allow students to emphasize the components that best suit their interests and learning style. Students are encouraged to work in teams of two (or more), with one student focused on computations and one focused on experiments (sharing figures with proper citations and acknowledgments). Students are also encouraged to work together when performing data analysis, error analysis, visualization,and illustration. All aspects of this course except for the writing or presentation of the project and the peer review, can be done collaboratively. Remember that it is critical that proper acknowledgement be provided when working collaboratively.

One key to experimental and computational physical chemistry is that there are often many different methods that can be used to address the same scientific problem. We encourage students to explore new methods and will always give added weight to students that go beyond following the exact procedures used in past labs. Independent research skills and independent exploration is always allowed and even encouraged in upper division laboratory sciences.

COMPUTATIONAL

- Use standard electronic structure-based quantum mechanics based computational methods or software to determine thermochemistry properties for several isolated 'gas' molecules. The goal is to do computational experiments to determine estimates of the heat capacity of several of the gases that would be looked at in laboratory experiments (e.g., Ar, N_2, O_2, CO_2, CF_3CH_2F). The computational methods will allow the contributions of translational, rotational and vibrational degrees of freedom to be individually computed. An example of a simple online browser-based tool for molecular computation is MolCalc (https://molcalc.org).[6] A more in-dept discussion of computational software is provided at the biopchem.education website and we are working on an advanced version of molcalc which students can access at molecalc.cloud. ASU online students should also have ASU computer accounts on Agave and access to WebMO and computational packages such at Gaussian for any advanced computation projects.
- The primary computational component for project 1 is the thermochemistry discussed in the first bullet point above. An additional component for extra credit or an advanced computational addition to project 1 is to explore atomic and molecular diffusion of the same gases discussed above. Specifically, use the kinetic theory of gases or standard molecular hard-sphere simulation packages or online apps to visualize and estimate the diffusivity of several of the gases that are associated with this laboratory project (e.g., Ar, N_2, O_2, CO_2, CF_3CH_2F). This can be done at a more advanced level by turning to molecular dynamics (MD) computational packages[7], for students that are interested in focusing on computational chemistry (and the experimental diffusivity can be omitted, if advanced MD simulations are performed). An example of a simple online simulator for diffusivity is PhET. An example of a good MD package is NAMD[8] or GROMAC[9], and more information can be found at the biopchem.org website.

EXPERIMENTAL

- Using acoustic interferometry, determine the speed of sound propagation for air and at least two pure atomic or molecular gases such as He, Ar, N_2, O_2, N_2O, CF_3CH_2F, or CO_2.[5] Use the experimentally determined sound velocity to calculate the heat-capacity ratios for the gases experimentally measured. The acoustic interferometry can be done as a DIY home lab, an ASU-Sync lab (with TA's assistance) or through asynchronous remote access and control data collection lab. For Spring 2023, the primary recommended method is the remote access and control of an acoustic interferometer that is setup and available at ASU for this ASU online lab. A critical component of this experiment is to first determine an accurate length of the tube for the experimental acoustic interferometer being used. This is commonly done using either Air or Argon gas, which as a very well know sound velocity. With an accuracy and precise determination of the acoustic interferometer tube length using a gas with a known speed of sound, all other measurements of various gases can use this determined length and an accurate and precise speed of sound can be determined.
- Using acoustic interferometry with a calibrated length, determine the speed of sound propagation for an unknown gas that will be provided for the remotely accessible instrument setup in the physical chemistry laboratory on the Tempe Campus at ASU. Use this sound velocity to determine the heat-capacity ratio for the unknown gas measured. From the remote experimental measurements and data analysis, determine as many thermochemical properties as possible and make a hypothesis about the molecular identity of the unknown gas.
- Ways to further explore and interrogate the property of gases using an acoustic interferometer, would be to look at the temperature dependences (or pressure dependence). The apparatus can also be changed and explored to better understand what parameters most effect the measurement. For example, the length of the tube, the diameter of the tube, the end cap materials, the speaker, the microphone, the type of input noise and data collection rates can all be systematically varied, and the effect of these changes explored (what optimizes the apparatus for sensitivity? Resolution?)
- The direct measure of gas diffusion can be measured in several ways, and most involve equipment that does not lend itself to DIY home lab or remote control. The sound speed and the diffusion coefficient are indeed conceptually different quantities; however, they can be related in ideal gases using the kinetic theory of gases (taught in introductory and physical chemistry). Experimental measurement of diffusion is an extra credit or advanced (Project X) additional component option for students.

DATA & ERROR ANALYSIS

- Make a figure with the molecular representations of the molecular gas(es) used for the computational experiments.[6,10] Further summarize the computational heat capacity and thermochemistry results in a table with a caption that provides a good summary of the computational details.[11–15]
- Make a figure with representative raw data obtained from the acoustic interferometry experiments and the sound spectrum (FFT processed data).[5,16–18] This can be included in the report or supplemental section (at the discretion of the student). Use the sound spectrum to determine at least 10 resonant frequencies for each gas at a known temperature (and/or pressure). Plot the resonance number versus resonance frequency and use a linear fitting routine (show the fit and provide the linear best fit values and R^2). This now allows the calculation of the speed of sound (from the slope of the linear fit). Optimized fitting parameters and associated errors for all gases and one or more known and measured temperatures (and/or pressures).
- Calculate C_P/C_V (γ) using the sound velocities determined in the step above. This should be done assuming an idea gas equation of state (EoS). As an extra credit and advanced component, students can use a more advanced equation of state such as the van der Waals (vdW) EoS.
- Translational, rotational and vibrational contributions can be determined through the computational exercise as well as classical and quantum theory. Also, a predicted C_V can be determined from idea gas and vdW gas equation of state assumptions.
- The emphasis of project 1 will be more on the thermochemistry and less on transport (diffusivity). However, at minimum all students should do some basic simulation of gas diffusion (velocity distribution and collision frequency – i.e., kinetic theory of gases) and either be given some experimental self-diffusion data (or look it up in the literature).
- The diffusivity is a direct measure of the translational degrees of freedom of the gas. This provides some molecular insight and visualization to one of the degrees of freedom responsible for contributing to the gas heat capacity. Making this connect and the relationship to the kinetic theory of gases is critical for relating the experiment to molecular theory.
- Use standard propagation of error techniques to report error associated with all measurements and subsequent calculations and data fitting.[2,19–22] All reported numbers should have the associated +/- error and units.

PROJECT REPORTS

The most traditional method used to communicate your laboratory project computational, experimental and associated analysis (data/error) is through a written laboratory (project) report. This handout provides an example of standard two column formatting, figure formatting, citations and referencing that is expected in a complete written report. There is also a report template that provides further explicit information to assist students with completing a properly formatted report with all appropriate content discussed. A rubric for evaluation of written reports is provided in the course syllabus. The following steps are suggested to students:

- Download a template and create a tentative title and add the author information.
- After reading this handout, perform a literature search and read and/or review some of the references. Start a tentative introduction of the written report with references (citations) before starting the computational, experimental or data analysis components of the project (lab).
- Plan 1 hour to make a first attempt at the computational component and associated data/error analysis. You should be able to immediately afterwards start an initial draft of the experimental section (subsection computational) and figures/tables associated with the computational components of the project.
- Plan 1 hour to make a first attempt at the experimental component and associated data/error analysis. You should be able to immediately afterwards start an initial draft of the experimental section (subsection 'remote experimental') and figures/tables associated with the experimental components of the project.
- It is common that after an initial attempt at computational and remote experimental 'experiments' that students will want to recollect data based on the initial data collected and analyzed. Plan another 1-2 hours for additional computational and/or remote experimental 'experiments' and revise figures, tables and analysis in an ongoing step-by-step progression of the written project report.
- With all the final computational and experimental data collected, work on finalized calculations and data analysis, much of which will be added to a supplemental information section of the report. Finally, review and complete an explicit error analysis component and propagation of error calculations, which are commonly reported in the supplemental information section.
- I recommend 'storyboarding' the results and discussion section of the report by first focusing on the creation and illustration of the objectives through figures with associated detailed figure captions (and to a lesser extent tables and table captions). Then the final component can be writing several paragraphs about the results and discussion that have been 'storyboarded' by the set of finalized figures (and tables).
- Typically, the final step is to complete the abstract, conclusion, and acknowledgement sections as well as making any final edits to the introduction (background) and references (citations) used throughout the various sections of the report.
- If chatGPT or any AI programs are utilized, please make sure it is explicitly discussed and cited. Also, students are encouraged to use modern hyperlinking in their reports.
- Lastly, it is recommended that all of this be completed 1-2 days before the due date and that students send their draft report to a fellow classmate or friends to proofread the report for typos and grammar before submitting.

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