Pchem 'Cloud' Project 1 - The Properties of Gases

ASU Online CHM343 – Spring 2022

Jeffery L. Yarger, School of Molecular Sciences, Arizona State University, Tempe, AZ 85287-1604.

* jeff.yarger@asu.edu

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 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 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. Students will be evaluated through their write-up of project reports which should take on the style used by scientific journal publications (e.g, *J. Physical Chemistry or J. Chemical Education*).

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).

Prof. Yarger designs online CHM 343 projects with 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

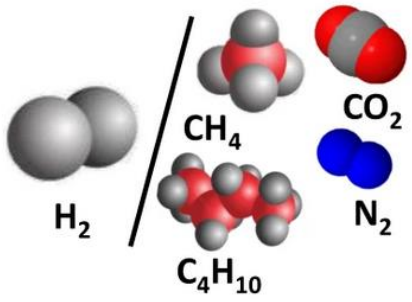

Figure 1 - Space filling model for several common molecular gases.

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.

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 welcome to work in teams of two, with one student focused on computations and one focused on experiments (sharing figures with proper citations and acknowledgments). In fact, it is encouraged that students work together when working on data analysis, error analysis, visualization and illustration. All aspects of this course EXCEPT for the writing of project reports and 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., He, N_2, CO_2 or Ar). 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.org website. ASU online students should all have ASU computer accounts on Agave (https://cores.research.asu.edu/research-computing/user-guide) and access to WebMO and computational packages such at Gaussian. This is highly recommended for completing the computational component of project 1. The ASU Agave computer cluster is designed for remote online access. The computing and data services have many getting started resources and online tutorials and help guides.
- 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 would be looked at in laboratory experiments (e.g., He, N_2, CO_2 or Ar). 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, or CO_2.[5] Use this sound velocity to determine the heat-capacity ratios for the gases measured. The acoustic interferometry can be done as a DIY home lab, an ASU-Sync lab (with TA's assistance) or a remote access and control data collection lab.
- Using acoustic interferometry, 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, data collection rates, etc can all be systematically varied and the effect of these changes explored (what optimizes the apparatus for sensitivity? Resolution? Etc)
- The experimental diffusion of gases can be measured in several ways, and most involve equipment that does not lend itself to DIY home lab or remote control. Hence, this will be done as an ASU-Sync lab and/or data will be collected off-line and provided.

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 8 resonant frequencies for each gas at each 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. Optimized fitting paraments and associated errors for all gases and all temperature (and/or pressures) should be determined and summarized in a table.

- Calculate C_P/C_V (γ) using the sound velocities determined in the step above. This should be done for two common gas equations of state, the idea gas law and the van der Waals (vdW) equation of state.
- 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 and either be given some experimental self-diffusion data (or look it up in the literature) or do at least a few diffusion experiments if the remote experimental setup is made available.
- 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.

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