

Chemical Engineering Thermodynamics: Transforming “Thermo” Lectures into a “Dynamic” Experience

Rebecca K. Toghiani
P.O. Box 9595
Department of Chemical Engineering
Mississippi State University
Mississippi State, MS 39762

Introduction

One of the more challenging subjects for engineering undergraduates is thermodynamics. From students' comments in both chemical engineering and other engineering disciplines at the three different institutions where I have taught, it is often viewed as 'voodoo' magic (the students' terminology) at worst and at best, limited in its applicability to problems they encounter in other courses. However, fundamental thermodynamic principles arise in so many areas of chemical engineering that a sound background in thermodynamics is of immense value to the undergraduate student. Providing the student with real world examples and applications of thermodynamic principles from other chemical engineering courses/concepts can help them to better integrate their understanding of thermodynamics with these other topics and affords them the ability to draw on this understanding to explore new and unfamiliar topics.

Most chemical engineering undergraduate curriculums require a two course sequence of thermodynamics. The first course generally focuses on the application of mass, energy and entropy balances to chemical and engineering processes. The second course generally entails an examination of non-ideal behavior – both for pure components and for mixtures, as well as phase and chemical equilibria. These courses are often steeped in theory (particularly the second course) and provide limited exposure to the specific applications in unit operations and in industry where these non-ideal effects are significant. If one were to poll undergraduates in chemical engineering, I believe that many would feel that their undergraduate training in this critical area of chemical engineering did not provide them with: 1) sufficient opportunities to examine applications where non-ideal behavior significantly impacts subsequent process design; 2) the ability to readily apply/incorporate the effect of non-ideal behavior as a function of process operating conditions in their subsequent unit operations and design classes; and 3) the opportunity to actually observe non ideal behavior in the liquid or gas phase.

The typical lecture format often utilized in these classes does not provide sufficient opportunity for students to visually observe the pertinent behavior that is described so well with mathematical formulae in their textbook. All of the chemical engineering thermodynamics textbooks available do present experimental data in graphical form; in some texts, extensive use is made of literature data in examples, explanations of phenomena and in end-of-chapter problems. These graphical representations and use of literature data in examples and problems can help students to integrate these concepts with material from other courses. A second method which can provide the opportunity to visualize various phenomena is through the use of in-class demonstrations and active learning experiences. Since the majority of students are visual learners

[1], these activities can significantly enhance the traditional undergraduate educational experience.

Active learning exercises and in-class demonstrations of non-ideal behavior and phase equilibria can be performed at little expense. While these demonstrations would not provide data of sufficient precision to be published in the literature, their use helps students to connect the underlying mathematical relationships to visually observed and experienced phenomena. This paper describes three such activities.

Background

The concepts typically covered in a first thermodynamics course include: PVT behavior of fluids (both ideal gas behavior and real gas behavior), use of thermodynamic property tables, the first law of thermodynamics, and the second law of thermodynamics. The primary focus in this first course is on pure fluids. Students have been exposed to the ideal gas law from their earliest adventures in chemistry and physics and thus, the use of this physical property model in solving thermodynamics problems is often a comfortable experience for them. Deviations from ideal behavior (i.e., the compressibility factor, the truncated virial equation, generalized correlations, simple cubic equations of state) are also fairly readily accepted and understood by students.

The steam tables are used as the platform for the introduction of students to thermodynamic property tables. Even though most CHE thermodynamics text books contain tables for common refrigerants in addition to steam, undergraduate students often do not realize that this type of data compilation is often available for many other substances, including some of the more commonly encountered hydrocarbons and refrigerants [2]. The same methodology can be used to extract properties from any of these tabular compilations, but students often fail to realize that they use the same approach to extract data and this extraction is independent of the fact that they have steam in one case and ammonia in another. Helping students to make these connections can benefit them immensely in their future endeavors.

The application of the first and second laws of thermodynamics generally involves utilizing a physical property model (ideal gas behavior or thermodynamic property table) to analyze a process given a set of constraints. Students become very conversant in simplifying the conservation of mass and the first and second laws of thermodynamics using keywords in the problem statement. While the primary focus of many of these problems is the evaluation of a certain process parameter (e.g., expansion work or heat transfer) and indeed, this is generally what we use as a means to evaluate student performance in a course. However, there is a certain responsibility on the part of the instructor to aid students in interpreting the result. This interpretation should include both a common sense analysis of the answer (i.e., negative absolute temperature or pressure don't make sense; expansion work should be positive – if we use the engineering sign convention, etc.) and also an inferential answer (i.e., for this turbine, the entropy change for the process is fairly large, what does this mean? This means that we will have to do a significant amount of work on the system to return the fluid to its original state). By including an interpretation when an example problem is worked in class, we aid our students in honing their expertise in this important aspect of problem solving. This can be extremely

beneficial to them in design courses where open-ended problems are the norm and they are required to critically evaluate process alternatives.

The topics covered in the second course are more diverse. At MSU, the second thermodynamics course focuses on: 1) thermodynamic relationships; 2) effect of pressure on thermodynamics properties (pure component, single phase); 3) solution thermodynamics (ideal and non-ideal liquid phase behavior, ideal and non-ideal gas phase behavior of mixtures); 4) phase equilibria (in all its permutations: VLE, LLE, VLLE, SLE, SFE, etc.) and 5) chemical equilibria. Faculty members are well aware of the connections between these topics and design/operation of reactors and separation equipment. At the undergraduate level, students often view these areas as separate and distinct, failing to grasp how closely related these subjects are. These topics, particularly the last three in the above list of five, are the bread and butter of the chemical engineer. In the classroom, we should facilitate development of our students' ability to integrate their understanding of thermodynamics with these topics unique to chemical engineering.

Demonstration #1: Deviations from Ideal Gas Behavior

One of the first topics students are exposed to in chemical engineering thermodynamics is deviation from ideal gas behavior. An active learning exercise modeled after a scenario described in a recent 'Random Thoughts' column by Felder [3] helps students to see why molecular interactions are so important in a gas under pressure. In his column, Felder describes a reactor design class in which the instructor is assisting students in performing an active learning exercise. Each student pretends to be one of two types of molecule in a chemical reactor. They simulate the chemical reaction when they (molecule A) bump into a molecule of type B by tossing a dice to see if they react with one another .

The effect of pressure (or conversely, increased density) on interactions between molecules in a gas can be readily demonstrated to students through a similar exercise. To implement, a large open area is needed (located at the center of campus, our drill field works great, but a large classroom with an open area will also work; the larger the area, the more students one can involve in the exercise). A rectangular region is marked off using tape or stakes/string. This region represents the volume in which the molecules are enclosed. The students who are assigned to serve as molecules are given basic instructions. They should move in straight lines until they bump into either another molecule or a boundary. At a boundary, they are reflected back into the volume at an angle equal to their angle of incidence. If they bump into another molecule, they collide elastically - turn 180° and move away at the same speed. Molecules are advised to keep a count of their molecular encounters (an alternative is to assign a pair of students to work together: one a molecule, the other a counter who observes and keeps track of encounters; roles can be switched for different scenarios given below). At the end of a prescribed time period, a tally can be made of the number of molecular encounters each student molecule experienced. Simulations can be conducted at low or high temperatures (student molecules move at a leisurely pace or a fast walk); under ideal gas conditions (only one or two students acting as molecules and rarely encountering each other or the boundary); or at higher pressure (more molecules placed inside rectangular area or same number of molecules confined to a smaller rectangular area). The influence of temperature and pressure on molecular

encounters can be examined through the tallies at the end of the exercise. Students clearly see how important molecular encounters become at higher density. The possibility of three students colliding becomes very real at these higher densities and these can be kept track of also. This exercise might take a little more time than required to lecture on the same material; however, students will never forget their life as a molecule or the lessons they learned about the effect of pressure and temperature on the behavior of gases.

Demonstration #2: Visualization of Liquid Phase Non-Idealities

The study of solution thermodynamics, in particular, liquid phase non-idealities, often begins with a discussion of excess properties and the Gibbs-Duhem equation. Non-ideal behavior in the liquid phase is extremely important in separation processes, in the design of storage drums, heat exchangers, and chemical reactors. Neglecting these effects during the design phase of a chemical process or unit operation can sometimes lead to the equipment failing to perform the desired function.

Undergraduate thermodynamics texts are particularly strong in solution thermodynamics and a number of essential topics are covered including: evaluation of partial molar properties (volume, enthalpy and excess Gibbs free energy) from experimental data and from a proposed model; thermodynamic consistency and use of the Gibbs-Duhem equation; calculation of mixture properties and phase equilibria given an appropriate model; and selection of an appropriate liquid phase model. As motivation for studying these topics, a simple in-class demonstration can be used to reveal to students the diversity of solution behavior that researchers have been examining for many years. I use this exercise as an introduction to non-ideal solution behavior and to provide a motivation for studying the phenomena.

Supplies for this demonstration are modest: three large beakers, a stirring rod and about 100-200 cc each of water, ethanol and toluene. Ethanol and toluene are commonly used in chemistry laboratories and thus are readily available on most campuses. For demonstration purposes, one can use food color in the ethanol or water to enhance the visual impact of the demonstration. Before any mixtures are prepared, the students (in groups of two or three) are asked to discuss and hypothesize what will happen when they mix: 1) ethanol and water; 2) ethanol and toluene; and 3) toluene and water. The class is polled and their guesses are tallied on the board. 50-100 cc each of water and of ethanol are mixed in a beaker. These are completely miscible with one another, and thus, form a single liquid phase. Next, 50 - 100 cc of ethanol and of toluene are mixed together. With the food color in the ethanol, students can actually see the mixing take place in the beaker and again, find that ethanol and toluene form a single, homogeneous liquid phase. When water and toluene are mixed, two liquid phases are formed. Even if the mixture is stirred up, it quickly separates into two phases. When asked if they have ever seen this phenomena before, some students quickly connect this behavior with that seen in the oil and vinegar dressing they put on their salads. The concept of partial miscibility can be introduced at this point as can the concept of a stable equilibrium state. What causes two phases to form when water and toluene are mixed and only a single phase to form when water and ethanol are mixed? This can lead into a discussion of the system seeking a configuration which minimizes the Gibbs free energy and maximizes entropy. This exercise has always served to stimulate students' interest in the diverse phenomena we are trying to model and describe

mathematically. The demonstration also helps them to begin to realize how extremely important it is to note limitations of proposed models and identify an appropriate physical property model which can adequately describe the phase behavior exhibited experimentally by a system.

In-Class Exercise: V^{EX} - Why Worry About This? A Custody-Transfer Case Study

Methyl *tert*-butyl ether, ethyl *tert*-butyl ether and *tert*-amyl methyl ether are chemicals which have experienced tremendous growth since the Clean Air Acts of 1990 were enacted. A literature review of the thermodynamic data available for these compounds revealed that limited data were available for the various mixtures which might arise in production and in use. Some of the earliest literature citations were for excess volume measurements of these ethers with the primary components in gasoline. Not surprisingly, these measurements had been performed by a major oil company. The data of Jangkamolkulchal et al. [4] form the basis for this in-class analysis problem.

When chemicals are transported from supplier to customer, the customer and the supplier want to ensure that each party is credited properly. The supplier wants to ensure that they are transferring a known quantity of material to the customer so that the customer can be properly invoiced. The customer wants to ensure that they are not shortchanged in the transfer process and that they are not having to pay for material that they do not receive. Thus, the supplier needs to be cognizant of the impact of liquid phase non-idealities for the system of concern in order to protect their interests and to also satisfy the customer. The densities and excess volumes of binary mixtures of the ethers and primary components in gasoline were measured and reported in the cited paper as were these properties for pseudo-binary mixtures of each ether with gasoline. The question posed to the students is: Given these data for the ether/gasoline mixtures, do non-ideal effects impact either the supplier or the customer adversely if ignored?

The students are provided with some information regarding reformulated gasoline including the EPA guidelines regarding the oxygenate content of RFG. The range of temperatures which might be experienced during material transfer is also provided. Students are provided with the mixture density as a function of composition and temperature as well as the pure component densities for the ethers and the density of gasoline. In order to answer the question, students must evaluate the excess volume from the experimental data and then perform an assessment as to the contribution of the excess volume to the mixture property. These calculations are fairly straight forward, entailing the definition of the excess volume ($V_{\text{mix}} - \sum x_i V_i$) as well as some unit conversions (density to specific molar volume).

An easy way to implement analysis of the data set in a classroom setting is to divide the class into groups of two or three students. All groups spend a few minutes working out the relationship between mixture density and specific molar volume. The groups are then polled and the developed relationship agreed upon by everyone and written on the board. The analysis of individual data points can be divided up among the student groups so that each group is working out an excess volume calculation for a single data point. The results of this second step can then be tabulated on the board, making them available to the entire class. Student groups can then examine the tabulated data with the instructor making sure that expected behaviors are observed in the calculated data. The final step in the exercise is to combine groups to form larger groups

of 4 to 6 students and have them discuss and reach a consensus response to the posed question. There can be a diversity of opinions when the consensus responses are tabulated and the instructor can then lead a discussion with the class through the critical points used to make their assessment. This exercise helps students to see a practical application of excess properties. It also makes them aware of concerns that suppliers and customers have when transferring material.

Conclusion

Using demonstrations and in-class exercises such as those described in this paper to facilitate student comprehension of thermodynamics topics can provide the students with a firmer understanding of the underlying concepts. Their use provides active learning experiences and a change of pace from the typical lecture format. Inclusion of these exercises can provide a stimulating environment and can increase student motivation towards the subject material.

References

1. Felder, R.M., Stice, J.E., Leonard, R., National Effective Teaching Institute, June 1994.
2. Felder, R.M., "The View Through the Doors", *Chem. Engr. Education*, 23(3), 166, 1989.
3. Reynolds, W.C., THERMODYNAMIC PROPERTIES IN SI: Graphs, Tables, and Computational Equations for 40 Substances, (Department of Mechanical Engineering, Stanford University, Stanford, CA: 1979).
4. Jangkamolkulchal, A., Allred, G.C., Parrish, W.R., *J. Chem. Eng. Data*, 36(4), 481, (1991).

REBECCA K. TOGHIANI is an Associate Professor of Chemical Engineering at MSU. A graduate of the University of Missouri-Columbia, she received the Dow Outstanding New Faculty Award (1996) and the 1997 Joseph J. Martin Award from ASEE. She was named a John Grisham Master Teacher at MSU in 1996. Her research interests focus on phase equilibria, membrane separation processes and thermodynamics of aqueous electrolytes.