CHALLENGES TO LEARNING AND TEACHING THERMODYNAMICS

John P. O'Connell
University of Virginia • Charlottesville, VA
California Polytechnic State University • San Luis Obispo, CA

When I was interviewing for faculty positions in 1964, I encountered at the University of Florida a delightful Texan named Frank P. May. He asked me, "So, what do you do?" I proudly responded, "Thermodynamics!" "Harrumph," he retorted, "Thermodynamics is a state of mind!"[1] May was not alone; even very recently Haddad said,[1] "No other discipline in mathematical science is riddled with so many logical and mathematical inconsistencies, differences in definitions, and ill-defined notation as classical thermodynamics." As I thought about May's description over many years of teaching the subject, I concluded it is a generally apt characterization, and saying it that way might help us appreciate why thermodynamics is so difficult for students to understand and utilize, as well as for their teachers to instruct about.

Twenty-five years ago, Don Woods organized an AIChE Annual Meeting Symposium and edited an issue of this journal on the "Knowledge Structure" of chemical engineering.[2] My contribution was on thermodynamics,[3] which Don confided might be the most difficult among the six subjects. A prominent, and still relevant, quote in the paper was, "Though thermodynamics focuses on natural phenomena, it is really just a deductive structure developed by creative and systematic human minds. Nature has carried out her diverse processes for eons without being explicit about energy, entropy, and fugacity."[3] Humans invented the obscure terms used to describe nature. No wonder the subject has become as Haddad[1] characterizes it.

John O'Connell *is professor emeritus of the University of Virginia and research scholar in residence at the California Polytechnic State University, San Luis Obispo, CA. He has a B.A. from Pomona College, S.B. and S.M. from MIT, and Ph.D. from U. Calif. (Berkeley). He was a faculty member at the University of Florida for 22 years and at the University of Virginia for 25 years before retiring at the end of 2013. His interests have covered molecular thermodynamic modeling for phase equilibrium and physical properties, especially for process design; molecular simulation of micellar structure and of fluid properties; adsorption and surface diffusion; chemical engineering education; and hydrophobic chromatography bioprocessing. His most recent work involves thermodynamic analysis and properties modeling of chemical processes, with a focus on entropy generation as a measure for comparing efficiencies and insuring property model consistency.*

Reference 3 shows several tables and figures on the development of the subject, and made suggestions about pedagogy; connections to them will often be made here. My present purpose is to share my more complete understanding about how the subject challenges thermodynamics learners and teachers, as well as to articulate more of my ways of dealing with the situation.

FIVE CHALLENGES TO LEARNING AND TEACHING THERMODYNAMICS

The challenges are listed here from fundamentals to practice. They cover the most important issues I have encountered. I think some may not normally be made explicit. This list is an extension of that in Table 9 of Reference 3.

Challenge #1 Scope and level. Thermodynamics may be humanity's grandest achievement for representing the behavior we experience in much of the natural world. This was recognized by such notable scientists as Einstein,[4] Gibbs,[5] Maxwell,[6] and Eddington.[7] Unfortunately, it probably takes their level of intelligence to fully grasp the meaning and implications of thermodynamics. We, of normal technical intellect, probably can hope to get only part of the meanings. How far can we get, given who we are?

Challenge #2 Mathematical abstraction. Thermodynamics is mathematical and abstract, rigorously logical, and based on conceptual (unmeasurable) properties (or conceptuals,

---

[1] *The rest of the story is that I asked Frank May what he did. He replied, "Process control." I rejoined with, "Process control is mysticism!" We were fast friends during and after the 22 years we were colleagues at Florida.*

for brevity), such as energy, entropy, fugacity, etc., that are distinct from measurables, such as volume, pressure, composition, etc. In the early 19th century, Carnot attempted to formulate the maximum work obtainable from a heat engine.[8] He labored under the false assumption that heat was carried by the intangible "caloric" fluid, but he laid the foundation for the Second Law. Joule's experiments dispelled that error, established that adiabatic work was independent of the process (unlike when heat is also involved), and connected the units of heat and work.[9] From these observations, Clausius and others[10,11] articulated the First and Second Laws. They identified the conceptuals, and fully articulated the thermomechanical Laws, which are "always true" when invoked consistently. Then, using only mathematics and graphics, Gibbs was able to extend these Laws to mixtures, multiple phases, and chemical reactions,[5] as well as to connect macroscopic thermodynamics to molecular theory.[12] Finally, in the early 20th century, Carathéodory[13-15] recognized that the Second Law, until then framed physically, could also be derived mathematically. My "Zeroth Law" is "All that mathematics we use works!"

It is not surprising that engineering teachers and learners are unable to fully appreciate such developments; compact, rigorous, and abstract logic may not be our strengths[2]. Thus, even with extended study, like the decades spent by the eminent researchers, those of us with only normal mathematical acumen might miss much of the content and efficiency of deductive application of the Laws. How much of these mostly mathematical elements can each of us absorb and use?

Challenge #3 An incomplete discipline based only on equations, not numbers. Admitting that "thermodynamics is necessary, but not sufficient" can be frustrating. Thermodynamics texts and courses give few, if any, details about transport phenomena,[17] reaction kinetics, or chemical processing. How can we have the stamina and patience to deal with thermodynamics, knowing there is so much more to come?

Further, the fundamental thermodynamic relations do not contain any numbers; they only define conceptual variables related via equations to each other and to measurable properties. Engineering applications demand calculations to obtain values, but these only appear when sufficient numerical values are put in. How can we, and our students, become fully comfortable with so much manipulation of variables and so little evaluation?

Challenge #4 Laws are always true; models are imperfect, but necessary[3]. Values of differences in conceptuals must be obtained by manipulating experimental data or putting models with parameter and property values into the relations. Connecting conceptuals to measurables can be hard work, especially because there are so many models. How do we distinguish the types of properties, avoid confusing "always true" fundamentals with "sometimes true" models, and select models to minimize error?

Challenge #5 Solving problems. Solving thermodynamic problems is often complicated. Problem situations are rarely framed in terms of the conceptuals in the Laws and their relations. Where in practice do the thermodynamic elements arise? The approach must be to rephrase the specifications in terms of fundamentals, do thermodynamic manipulations, and only then compute the desired results. Rather than following this intricate process, teachers, textbooks, and students often just tabulate formulae for many different cases, leading to misconception and error, particularly when the assumptions made in developing the formulae are not explicit[4]. What might be an efficient and reliable approach to problem solving in thermodynamics, and do we have the discipline to use it?

SOME SUGGESTIONS TO MEET THE CHALLENGES

It took many years of experience for me to arrive at the present suggestions, which build on, and extend, those in Table 10 of Reference 3. The relatively recent literature on active learning[19] and caring about students,[20] seems to reinforce these approaches. Not all my suggestions can be done in the restricted time of a single course, but they are offered here for teachers to select which they, and their learners, might find effective. Suggestions are numbered in correspondence to the challenges.

Suggestion #1a Admit it is hard. While attaining full proficiency of the subject within the time allotted is unrealistic for most teachers and learners, we should still try to maximize understanding, which is highly individualized. Early in the course, I tell my learners that I took five courses in thermodynamics, but it was not until the third time I taught it that I became "mostly comfortable" (my definition of "understanding") with the subject. Yet, after more than 40 years of teaching the subject, I still could find new ways to mess up presenting its formulations and using them in problem solving. Thus, they would know that I "felt their pain," but also that we could not allow that to deter us from going as far as we could. There is great power in mastering even some of the discipline. If each learner gained new insights and tools from the study, it would be worth it.

Suggestion #1b Vary the learning experiences. Our diversity of intellectual strengths and learning styles means that a

---

[2] *We need not feel badly. H. Bumstead*[16] *wrote, "It is universally recognised that [Gibbs' third paper] was an event of the first importance in the history of chemistry. ... Nevertheless, it was a number of years before its value was generally known, this delay was due largely to the fact that its mathematical form and rigorous deductive processes make it difficult reading for any one, and especially so for students of experimental chemistry whom it most concerns...."*

[3] *G.E.P. Box said,*[18] *"all models are wrong, but some are useful." I prefer the less disparaging word "imperfect," and insist that engineering work demands implementing appropriate models.*

[4] *I often quote the Law of Suspended Judgment,*[21] *"Assumption is the Mother of all screw-ups."*

uniform approach will not maximize collective student accomplishment. Thus, the course should provide a variety of learning experiences and assessment techniques to best meet as many individuals' needs as possible. In particular, I try to articulate the course goals. Nowadays, I would phrase those as "To have the confidence to recognize the thermodynamics of a situation and to use its tools in obtaining an engineering solution." The first day, student pairs would complete a diagnostic quiz to reveal their math skills and to uncover misconceptions about the subject from earlier courses and experiences. As Ausubel said,[22] "The first influence on learning is what the learner already knows. Ascertain this and teach accordingly." Exposing the variations in background and knowledge was quite informative and guided both my and the students' approaches.

Suggestion #1c Have small group interactions with student participation. Early on, I found great benefit from scheduling sessions with smaller groups of students, similar to the format I had at MIT in 1960 of 1–2 larger lectures and 2–3 smaller recitations each week. The latter had explicit agendas and sets of questions to be addressed by oral student responses. Later, using remote response devices, I could find out in full classes how well the material was being grasped. With instant feedback, we could move ahead—or not. Further, these graded interactions kept students engaged.

T.C. Scott and I created workshops with real equipment and visits to University of Virginia facilities (UVa), where students were assigned to observe, analyze, and discuss carefully tailored situations.[23,24] One particularly effective series of exercises was to recognize the fundamentals of "pumping heat," that is, to appreciate the Second Law statement that work is needed to do something nature does not do spontaneously. Taking in heat at lower temperature and putting it out at higher temperature requires work. Also, technology uses different means and scales for accomplishing such a process. Students had 1-hour workshops on heat pumps with different heat transfer sources and sinks (air to air, water to air, liquid to liquid) via instrumented window air conditioners, a modern refrigerator (including identifying both its essential and its "convenience" features), a drinking fountain, and a UVa chilled-water system. The last involved donning safety equipment and visiting a large-scale operation. The students would find and record letters that were put on paper strategically posted around the facility and on important equipment that corresponded to names in the pre-read material. Proper identification would spell out the message, "thermodynamics is everywhere," which, when students figured it out, led to wonderful student-teacher interactions. Touring the system's evaporative cooling towers was always the highlight.

I also had student pairs/trios present brief (three slides, 5 minutes) summaries of what they got out of the previous class and where they observed connections to thermodynamics in their lives of the preceding week. Part of the exercise included another group being assigned to ask questions of the presenters. All performances were graded by both teacher and students.

Suggestion #1d Assess wisely. Progress through the subject is highly nonlinear. This means doing periodic assessments for the teacher and learners to know how things are going, to engender patience with the process, to provide insights about gaps in each learner's path, and to build confidence that progress occurs. Some students failed the first time through the course. When they came around again, they often made astonishing advances; "soaking time" seems to help. The graduate textbook by Jim Haile and myself starts from the very beginnings to recognize this effect.[25]

Here are a few suggestions for assessment. Present relations students must identify as "always, sometimes, or never" true. Give short, closed-book, multiple-choice quizzes about property definitions and relations to instill the essentials. Assign only a limited number of homework problems that require calculations, augment these with more complete projects. (My courses included a project to introduce Aspen Properties® by having student pairs describe vapor-liquid equilibrium and properties of assigned binaries of components and compare the results with the literature.) To make quiz calculations quickly accomplishable, employ only ideal gases and ideal solutions, and then also ask for the expected effects of reality ("up, down, no change?"). Choose some problems where the basic expressions are not formulae to be memorized, so some derivation, even as simple as eliminating terms, is necessary. Include questions about fundamentals arising in the workshops. Pose troubleshooting cases whose analyses involve thermodynamic effects (check with your design teacher for these).

Suggestion #2a Use math at the lowest feasible level. There are an almost overwhelming number and variety of elements of the subject, as shown in the complicated image of Figure 1 in Reference 3. As a result, minimization of both total content and obfuscating details is important. Connect the material to learners' experiences (which we want to increase) by remaining at the lowest possible levels of mathematics: multivariable differential and integral calculus, differential equations only to distinguish exact and inexact differentials, and multiequation algebra. Using more math is merely intimidating, although admittedly necessary for connecting to transport phenomena.[17] To enhance understanding and the value of generalizations, use analogies and similarities as with transport phenomena.[26]

Suggestion #2b Distinguish types of variables. Regarding properties, be honest about why conceptuals are defined; it's so that mathematics can be applied to compactly describe, through derivation, all the phenomena covered by the Laws of Thermodynamics. Nature's processes of heat and work involve inexact variables, with differentials signified by δ. It is best to connect them to differences in properties, *i.e.*, from integration of exact differentials, signified by d.

Table 1.
Elements of the Laws of Thermodynamics

Law	Defined Variables	Defining Equations	Always True
First	E_{sys}, Q_b	$dE_{sys} \equiv dW_{b\,adiabatic} \equiv \delta W_b + \delta Q_b$ (1a)	$\int dE_{sys} = 0$ (1b)
Second	S, S_{gen}	$dS \equiv dQ_{b\,rev} / T_b \equiv \delta Q_b / T_b + \delta S_{gen}$ (2a)	$\delta S_{gen} \geq 0$ (2b)

Suggestion #2c Develop the Laws in similar ways. The First and Second Laws have two elements: (1) define a conceptual, and (2) state an "always true" behavior of the conceptual as shown in Table 1. Eq. (1a) defines the system energy, E_{sys}, and then defines heat, Q_b, which crosses the boundary of a closed system due to temperature differences. It is assumed we know about work crossing the boundary, W_b, although Redlich was not so sure about that.[27] The first definition is from Joule's studies giving adiabatic work independent of the process, making it a state property[9] (the differential is d, not δ). If heat is involved, the process proceeds with the inexactness of the process W_b canceled by that of Q_b. Eq. (1b) says that energy is conserved.

My way of interpreting the First Law is "With energy, like mass, you cannot get something for nothing, *and* you cannot throw it away." (I then show an image of a power plant where the biggest units are for disposing of the 2/3 unused input energy that must go to the environment.) Of course, this requires defining a system and, especially, its boundaries. Also, since E_{sys} is a "property," its characteristics should be explained in physical terms, not just with math.

Eq. (2a) defines the entropy, S, the entropy generated, S_{gen}, and the temperature at which the heat crosses the system boundary, normally at the exterior, T_b. Carathéodory[13-15] showed that there must be an integrating factor for the inexact differential $(\delta Q_b)_{rev}$ to give an exact differential, dS. Eq. (2b) allows one to derive nature's invariably observed phenomena such as heat flowing from high to low temperature, and not all the heat input to a process can be converted to work. My way of interpreting the Second Law is "Nature does many things spontaneously; going against these will cost you, with the only issue being how much." To help appreciate the meaning of the variables, note that S_{gen} is from the irreversibilities of all real processes, and that efficiency is better when S_{gen} is less. Experience shows S_{gen} increases with (1) higher temperature differences over which Q_b flows or mixing occurs, (2) greater pressure differences that cause deformations and fluid flow, (3) larger concentration differences in material transport, and (4) faster process rates. The first three effects are in the general order of impact.

The power of Eqs. (1) and (2) is that they give the universal constraints on heat and work flows for every known terrestrial process. Of course, these do not directly connect to any process, so more steps are required. The important point is that regardless of what is done, these relations, and any derived from them by mathematics, must always be obeyed.

Suggestion #2d Build confidence in working with conceptuals. The next step is to integrate the differentials, meaning that absolute values cannot be obtained for E, S, or any other conceptuals related to them. This also leads to using reference states defined in the "fine print" of tabulations. Then, to connect to real processes, we evaluate differences in conceptuals from variations of measurable properties for the process states (see below). Part of this procedure is to define new conceptuals so formulations and evaluations appear to be simpler. Thus, Gibbs energy, G, is defined because its natural variables of T and P are convenient, and internal energy, U, is defined by removing the often inconsequential kinetic and potential energies (exact differentials) from E_{sys}.

We should introduce only those conceptuals necessary for undergraduate engineering problems and limit the number of relations among them. For example, there are at least 15 Maxwell relations generated from the independent order for taking second cross derivatives of the usual conceptuals (U, H, A, G, S) with respect to measurables (T, P, V). Physical chemistry courses often require students to know all of them. In practice, only two are essential; they connect variations of entropy with volume (3a) and with pressure (3b) to variations in only measurables,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V > 0 \tag{3a}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P < 0 \tag{3b}$$

I try to connect such relations to experience. For example, the entropy derivatives of Eqs. (3) have signs that never change. Thus, when volume increases or pressure decreases at fixed temperature, entropy always increases. From other considerations, the derivatives of S with respect to T at fixed P or V are always positive, so S also always increases when T increases. Thus, we may not know "what entropy is," but we can know "how it goes." The Gibbs-Helmholtz equations that connect G to H and A to U are important additional relations. Haile and I[25] use the term "response functions" for such derivatives, and we classify derivatives in terms of their usefulness based on the number of conceptuals in them (Eqs. 3 have only one, S. We consider Maxwell relations with more than two conceptuals to be impractical and not worth learning).

While Legendre transformations rigorously and compactly define new conceptuals, I omit this methodology. We use few new properties and find that most students prefer to memorize their definitions rather than derive them. Whenever an important equation is presented—either derived or merely stated—I try to walk through the terms explaining their significance and note how they should be treated in applications. Examples include the significance of kinetic and potential energy terms compared to the internal energy in the First Law equation[5], and determining the pressure range to include the Poynting Factor in a liquid fugacity calculation.

A final aspect of working with conceptuals is to write Eq. (1a) in terms of only exact differentials. Eliminating kinetic and potential energies, and considering only PV work, we find:

$$dU = \delta W_b + \delta Q_b = \delta Q_{rev} + \delta W_{rev} = TdS - PdV \qquad (4)$$

where the first equality is for all processes, the second—from U being a state property—applies to reversible changes, and the last comes from substituting the definitions. If there are other "orthogonal" effects such as from surfaces, size, composition, electric fields, etc., they are formulated in terms of coefficients and differentials of state properties and added to Eq. (4).[27]

Suggestion #2e Emphasize open systems. So far, only closed systems at constant composition have been considered, as in physics and chemistry. Engineering systems have boundaries open to material flow and have mixtures that cause complications. I try to proceed with a minimum of definitions and relations. System boundaries and ports of material entry and exit should be found first. I usually force students to draw their own system diagrams, a skill they ultimately find very helpful. The First and Second Laws for open systems can be written in the form of the "stuff equation"[25]

$$\text{Stuff}_{in} - \text{Stuff}_{out} + \text{Stuff}_{generated} - \text{Stuff}_{consumed} = \text{Stuff}_{accummulated} \qquad (5)$$

where thermodynamic "stuff" can be mass, moles, energy, or entropy, with some terms in Eq. (5) being zero for some "stuffs." The signs here are chosen so each stuff is positive. For mass and energy, no generation or consumption ever exists. For entropy, there is generation but not consumption. All terms can exist for moles of chemical reaction systems. For closed systems, there are no "ins" and no "outs," so Eq. (5) still applies. For open steady systems, there is no accumulation, and the quantities can be either rates or amounts over time. Students seem to appreciate having the major relations in this single form.

Assigned problems may ask which terms are present in the stuff equations for energy and entropy with the material balances already built in. A well-posed problem specifies values for all but two of the variables in the equations, and these must be found. Note that conceptuals can be functions of several variables. I create problems where students just determine if there are enough, too few, or too many specified variables. I demonstrate that many problems can be created for the same system, and thus precisely the same equations can be used, leading to different answers from different variable or numerical specifications. Sometimes I ask students to create their own problems in this manner. The idea is to reinforce that remembering a few general equations is much easier than keeping track of many specific formulae.

Suggestion #2f Justify the complexities for mixtures. There are two new aspects appearing with mixtures. One is that their properties are not normally simple sums of pure component properties. I show that behavior with an in-class demonstration, where suitably garbed students (with safety glasses and rubber gloves) pour 50 ml of methanol and 50 ml of water into a 100 ml graduated cylinder. I first ask the class to vote whether the mixture volume will be more, less, or equal to 100 ml, and if the mixture will feel warmer, cooler, or the same temperature as the pure components. The observed, and often unexpected, smaller mixture volume and higher mixture temperature help justify the messy formulation of partial molar properties. The second aspect is to account for the known effects of composition on energy and entropy by adding terms to Eq. (4). Here, mathematics provides the rigor, and since the added terms contain partial molar properties, they are again justified.[25]

Suggestion #2g Treat both phase transfer and equilibrium. Chemical processes with distillation, extraction, chromatography, etc., offer opportunities to demonstrate the power of thermodynamics. Toward the end of my teaching, UVa ChE chose to replace half of the second thermodynamics course on mixtures plus phase and reaction equilibria with an introduction to separations. This meant that applications of driving forces in nonequilibrium systems—which are often not treated in thermodynamics courses but are vital to know about—and the uses of phase equilibria (VLE, LLE, adsorption, etc.) could be shown immediately after doing derivations. Also, the terminology of processing was established ahead of the transport and operations courses.

The path from Eq. (2b) to driving forces is tortuous because it can involve lengthy derivations for stability. Usually, I direct students to the development elsewhere and just cite the end results, emphasizing that property extrema at equilibrium are subject to system constraints. Thus, entropy is maximized only in isolated (fixed U, V, N) systems[6] and G is minimized only in isothermal, isobaric systems. I also point out that an important formulation is identification of the partial molar Gibbs energy as the chemical potential, μ_i. If not blocked, species transport is from a location of higher μ_i to lower μ_i (hence the property name, "potential"), while equilibrium appears when the system has the same μ_i everywhere, including in all the observed phases. It is important to emphasize that concentration and chemical potential are not always the same. The final step notes that μ_i diverges in the limit of infinite dilution of component i, so it is convenient for calculations to use a substitute: the fugacity, f_i, with the same driving force and equilibrium attributes as μ_i. Note that f_i is a conceptual

---

[5] *A fun problem is "if, instead of global warming, the accumulated energy for atmosphere temperature increase were converted into wind, how fast would it blow?"*

[6] *The value of S is lower for an ambient 2-phase system of oil and water than if it were a single phase!*

(not a measurable), it is not a "corrected pressure" (as is often taught), and its driving force behavior is embedded in its name's Latin origin, "fugit."

Suggestion #3 Work toward getting numbers. During development of the many properties and equations, when should experimental and calculated property values, especially of conceptuals, be brought in? Even if students have been exposed to steam tables and equations of state for pure components in prior courses, it is important to show how tables are obtained from correlation of many properties with an equation of state and what to do when tables do not exist for uncommon chemicals and mixtures. My problems either use tabulated properties or require giving the expressions used for calculations (as many unknowns as equations), and include a few calculations with ideal systems or with first-order nonidealities for gases and liquids (see below). In addition, the practical consequences of the Gibbs-Duhem equation are given; it is an inconvenient, but rigorous, differential relation among all the partial molar properties, T, and P that reduces the number of these apparently independent variables. All of these elements are introduced before doing phase and reaction equilibria. The tables of Reference 3 show this ordering.

The thermodynamics of reactions is probably one of the least understood outcomes of many thermodynamics courses, often because it is taught hurriedly at the end. Introducing it before phase equilibria can be more effective. There are too many details to show here, but the main principles are that stoichiometry links the initial amounts of components to the amounts of the species at specified extents of the independent reactions, and that equilibrium is reached when the reactions' affinities (related to species chemical potentials) become zero. (Note the distinction between components and species.) I show students how to determine the number of independent reactions, followed by creating a table with columns of species names, stoichiometric coefficients in different reactions, initial amounts, and relations for final amounts and for mole fractions from extents of reactions. This template clearly displays the essential information for solving reactor systems. Finding equilibrium extents of reaction can be difficult. I illustrate a standardized procedure of setting the exponential of reference state properties to temperature-dependent equilibrium constants, which are products of pressure and mole fraction-dependent fugacities, that leads directly to equation(s) to be solved for unknown equilibrium extent(s) of reaction. One outcome of insisting upon working with these equilibrium constants makes explicit that the final compositions, via extents of reaction, vary with pressure in a well-defined manner when temperature is fixed. My homework problems are often for ideal gases and ideal solutions, along with asking about the effects of nonideality and of changing T or P.

For equilibrium among phases α, β, etc., we use $f_i^\alpha = f_i^\beta = \ldots$ and then illustrate the five ways [the "Five Famous Fugacity Formulae (FFFF)"[7]] different quantities are combined to expose the measurables that are to be specified or found from solving the equation(s). I always try to make the dependences on measurables explicit. For example, FFF #1 for vapors or for liquids is $f_i^V(T,P,\{x\}) = x_i P \phi_i(T,P,\{x\})$, where formulae exist to compute the fugacity coefficient, ϕ_i, with an equation of state, noting the ideal gas value of unity. I point out that if one believes that the chosen equation of state model works for liquids (but cannot be used for solids) and properly traverses the vapor-liquid 2-phase region, the other four formulae are not needed. However, in the usual absence of such a model, alternatives have been developed. For a liquid component, i, below its critical temperature, FFF#5 is $f_i^L(T,P,\{x\}) = x_i \gamma_i(T,\{x\}) \phi_i^{sat}(T) P_i^{sat}(T) \left[PF(T,P,\{x\})\right]$, where γ_i is the activity coefficient and PF is the Poynting Factor. I always use models for the excess Gibbs energy, G^E, to obtain activity coefficient expressions, since then the Gibbs-Duhem equation is automatically satisfied. For ideal solutions, $G^E = 0$ and $\gamma_i = 1$ at all compositions. With the FFFF, students can then learn rules about which formula would best be used in various situations. A useful exercise is to show what approximations are embedded in FFF#1 (vapor) = FFF#5 (liquid) to yield Raoult's "Wish" (where $\gamma_i = 1$) and "Raoult's Law for Grownups"[8] (where $\gamma_i \neq 1$).

Suggestion #4 Use illustrative models and consistency tests. When relations among the variables for a given physical system (a problem) are written, it is important to know where assumptions and approximations have been introduced. At one level, detecting them is simple. If no conceptuals are present, models have been introduced. It is not so clear whether any models are embedded when some conceptuals are present, but a clue can be if parameters or properties, such as critical temperature and pressure, have appeared. Students should also have to estimate the likely signs and magnitudes of errors from imperfect models, as well as the uncertainties from variations in fitted parameters and experimental data. While these can be done with rigorous statistical analysis, alternatives are to do "what-if" sensitivity calculations by changing incrementally a parameter or property value and displaying the outcome, and to compare results from different models. Spreadsheets and process simulators are good tools for such exercises. Cases with both low and high sensitivity are valuable to know about. I find contrasting the compressibility factor (z) and fugacity coefficient (ϕ_i) from ideal gases and second virial fluids, as well as f_i^L from ideal solutions and the Porter model ($G^E = A(T,P)\, x_1 x_2$), are relatively easy to do and give students a feel for behaviors.

Data are often inconsistent.[28] Engineers must be aware of that, and should know how to use thermodynamics for

---

[7] *This phrase originated with M.M. Abbott of Rensselaer Polytechnic Institute.*

[8] *This phrase also originated with M.M. Abbott of Rensselaer Polytechnic Institute.*

testing. The most common test is for TPxy vapor-liquid equilibrium data using the Gibbs-Duhem equation. However, other tests of limits and continuity can be invoked.[29] Introducing data treatment activities can reveal real life.

Suggestion #5 Require using a Problem-Solving Structure. Often, the hardest part of solving problems is determining what the problem is and how to logically go from there to the desired results. Further, thermodynamics may arise in subtle ways. Thus, in addition to knowing a structure for the knowledge, following a structure for solving problems is valuable. Templates for thermodynamics have some unique aspects for reliable implementation. Haile and I developed the six-step "Problem/System/ALways-true/Model/Solve and check" (PSALMS) method of Table 2 (Table 8 in Reference 3), loosely based on the McMaster University Problem-Solving Program.[30] Getting students to always apply the process was sometimes difficult because it is too laborious for simple problems. Posing and solving complicated problems helps justify the procedure. I often show, and also assign, word problems with answers being the listing of the relations from only the PSALM steps, which could then be solved numerically. Not all students needed this practice, but enough did to make it worth doing.

Table 2.
The PSALMS Problem Solving Method

Problem	- Desired quantity, other variables
System	- Physical and chemical situation Diagram? Contents and constraints Boundaries, work modes, species/components Total variables, specified variables
ALways True	- Relevant generalized relations for specified system Balances on mass, energy, entropy Property differences Fugacity, reaction equilibrium constant equations
Model	- Approximations to generalized relations Choice of Famous Fugacity Formula If FFF # I, EOS Type Ideal, Virial, CSP, "Full (multiphase)"; P or V Independent If FFF #2-5, Reference State, Pressure Effect Specific choices, *e.g.* CSP parameterization; Cubic EOS; f_i^0 values; G^E correlation, group contribution method Data (new or literature)
Solve & check	- Analytic, graphical, tabular, numerical

CONCLUSIONS

Late in my career, I recognized the Law of Suspended Judgment[21] applies to the first day of classes. So, I would begin with a take-home survey to find out more about my students. It included, "What are your assumptions about yourself and about your teacher?" I was stunned when I once got back, "I expect my teacher to make everything easy to understand." The class and I immediately discussed this situation, starting with "What if it can't be made easy to understand?" followed by, "Actually, what do you mean by 'understand'?[9]" and giving my definition suggested above. After we considered the situation, I was able to ask, "Are you willing to work in your own way to overcome the challenges, so that you can make significant progress in your own understanding?" Many students responded positively to this inquiry and then proved their commitment. Only now do I think that explicitly listing the challenges for my learners might have facilitated even more effective discussion. Fortunately, however imperfect the conversations were, I believe they allowed implementing the suggestions given here, helped make my courses among the favorites of many students (at least that's what many, and some incredulous industrial recruiters, told me), and provided substantial intellectual and professional growth for most of my learners.

ACKNOWLEDGMENTS

I am extremely grateful to Professor J.M. Haile, currently of Macatea Productions, Central, SC, for stimulating many insights about thermodynamics education, some of which are given here, that we put into our graduate textbook,[25] and he included in his undergraduate text.[32] I also learned much from T.C. Scott, laboratory professor of UVa Mechanical and Aerospace Engineering (retired), with whom thermodynamic workshops and practical assignments were enjoyably developed. Finally, Robert Hanlon of MIT provided important references about the history of thermodynamics.

REFERENCES

1. Haddad WM (2017) Thermodynamics: the unique universal science. *Entropy* 19:621-691.
2. Woods DR (1993) Knowledge structure. *Chem. Eng. Ed.* 27(2):78.
3. O'Connell JP (1993) Thermodynamics: a structure for teaching and learning about much of reality. *Chem. Eng. Ed.* 27(2): 96-101. <http://ufdcimages.uflib.ufl.edu/AA/00/00/03/83/00118/AA00000383_00118_00096.pdf>
4. Klein MJ (1967) Thermodynamics in Einstein's thought. *Science* 157(3788):509-515.
5. Donnan FG (1925) The influence of J. Willard Gibbs on the science of physical chemistry. *J. Franklin Inst.* 199:457–483.
6. Maxwell JC & Pesic P (2001) Theory of heat (Dover ed., Dover Publications, Mineola, NY).
7. Eddington AS (1935) The nature of the physical world (MacMillan, London). Replica edition (1981) ISBN0-8414-3885-4 (University of Michigan, Ann Arbor, MI).
8. Carnot S & Mendoza E (1988) Reflections on the motive power of fire: and other papers on the

---

[9] *See the series of papers, "Toward Technical Understanding" by J.M. Haile[31].*

second law of thermodynamics by É. Clapeyron and R. Clausius (Dover Publ., Mineola, NY).

9. Forrester J (1975) Chemistry and the conservation of energy: the work of James Prescott Joule. *Stud. History Philosophy Sci.* 6(4):273-313.
10. Clausius R (1879) The mechanical theory of heat (MacMillan, London).
11. Kragh H & Weininger SJ (1996) Sooner silence than confusion: the tortuous entry of entropy into chemistry. *Hist. Stud. Phys. Biolog. Sci.* 27(1):91-130.
12. Gibbs JW (1902) Elementary principles in statistical mechanics (Charles Scribner & Sons, New York).
13. Carathéodory C (1909) Untersuchungen über die Grundlagen der Thermodynamik. *Math. Ann.* 67:355-386.
14. Kestin J (1979) A course in thermodynamics, vol. 1, revised printing, (Hemisphere Publishing Corp., New York).
15. Chandrasekhar S (1958) An introduction to the study of stellar structure (Dover, New York).
16. Bumstead HA (1903) Josiah Willard Gibbs. *Amer. J. Sci.* 4:XVI.
17. Swaney RE & Bird RB (2017) A connection between transport phenomena and thermodynamics. *Chem. Eng. Ed.* 51(2):83-87.
18. Box GEP, Launer RL & Wilkinson GN (1979) Robustness in the strategy of scientific model building in *Robustness in Statistics* (Academic Press, New York) 201–236.
19. Prince M (2004) Does active learning work? A review of the research. *J. Eng. Ed.* 93(3):223-231.
20. Felder RM & Brent R (2009) The 10 worst teaching mistakes lI. Mistakes 1-4. *Chem. Eng. Ed.* 43(1):15-16.
21. Wethern's Law of Suspended Judgment quoted at <https://schneide.wordpress.com/tag/wetherns-law/>.
22. Ausubel DP (1968) Educational Psychology: A Cognitive View (Holt, Rinehart and Winston of Canada Ltd, Toronto).
23. Scott TC & O'Connell JP (1999) Experiments to accompany a first engineering thermodynamics course. *ASEE Annual Conference Proceedings* 2333-2342.
24. Scott TC & O'Connell JP (2000) Workshop exercises for connecting fundamentals to equipment in the first thermodynamics course. *ASEE Annual Conference Proceedings* 6929-6938.
25. O'Connell JP & Haile JM (2005) Thermodynamics: fundamentals for applications (Cambridge University Press, New York).
26. Bird RB, Stewart WE & Lightfoot EN (2006) Transport phenomena, Revised 2nd Edition (John Wiley & Sons, Hoboken, NJ).
27. Redlich O (1968) Fundamental thermodynamics since Carathéodory. *Rev. Mod. Phys.* 40:556- 563.
28. Kim SH, Kang JW, Kroenlein K, Magee JW, Diky V, Muzny CD, Kazakov AF, Chirico RD & Frenkel M (2013) Online data resources in chemical engineering education: impact of the uncertainty concept for thermophysical properties. *Chem. Eng. Ed.* 47(1):48-57.
29. Kang JW, Diky V, Chirico RD, Magee JW, Muzny CD, Kazakov A F, Kroenlein K & Frenkel M (2014) Algorithmic framework for quality assessment of phase equilibrium data. *J. Chem. Eng. Data* 59:2283–2293.
30. Woods DR, Hrymak AN, Marshall RR, Wood PE, Crowe CM, Hoffman TW, Wright JD, Taylor PA, Woodhouse KA & Bouchard CGK (1997) Developing problem solving skills: the McMaster problem solving program. *J. Eng. Ed.* 86(2):75-91.
31. Haile JM (1997) Toward technical understanding. *Chem. Eng. Ed.* 31(3):152-157; (1997) 31(4):214-219; (1998) 32(1):30-39; (2000) 34(1):48-54; (2000) 34(2):138-143.
32. Haile JM (2002) Lectures in thermodynamics, Vol.1 (Macatea Productions, Central, SC). ❐