THE CHEMICAL ENGINEERING

APPROACH TO ENTROPY

Views of A Non-Thermodynamicist

James L. Throne
Assistant Professor of Chemical Engineering
Ohio University, Athens, Ohio

In a recent article (2), Bates sets forth some "canonical statements" in an attempt to clarify some of the irrational concepts and misleading labels which have evolved with thermodynamics, probably beginning with Black and the concept of "calorics" (5). I wish to take issue not only with Bates' approach to the healing of thermodynamics, but with the entire philosophy of teaching thermodynamics on the undergraduate-first year graduate level. In this paper, I would like to present what might be called a "non-thermodynamicist" viewpoint to the problems of teaching thermodynamics, my focal point being the concept of entropy and its abuse in chemical engineering. In a subsequent paper, I intend to present a course outline for thermodynamics on, say, a first year graduate level in chemical engineering. Such a course has been taught successfully at Ohio University by non-thermodynamicists.

Forests and Trees

While Bates' arguments regarding misconceptions and irrational nomenclature are well taken, I am not convinced, first, that his introduction of another set of nomenclature (regardless of its rationality) is "first aid," and second, that even if adoption of a standard set of symbols, definitions, axioms, canonical statements, and what have you, does take place (highly improbable, when, for example, Tribus (1) introduces, through information theory, concepts such as "temper"), that this type of first aid will not result in direct application to thermodynamics of the old saw, "the operation was successful, but the patient died."

I think that the dying patient, which I prefer to call mechanical thermostatcs (bowing to Tribus' careful definitions here), needs radical surgery, transfusions, and miracle drugs rather than simple first aid. Perhaps the time has come for the engineer who utilizes thermodynamics (in its true sense, i.e., transport of heat, mass, and momentum) in his work with physical and chemical phenomena (and here it must be understood that I am referring to a much greater scope of problems than those outlined by Bird, Stewart, and Lightfoot (3)) to render advice and, if necessary, to step in and perform the necessary surgery himself. It may well be that those who now apply first aid may see only single trees where entire forests (mostly unexplored) lie waiting.

Philosophy and Thermodynamic Concepts

As is well known, there are two major ways of approaching the developments of the major corner-stones of thermodynamics: through classical or macroscopic developments and through "statistical" or molecular developments. Both paths originate in physics and both require the person following the development to make some form of idealizing assumption. While I will have more to say on this point in the subsequent paper, I want to point out two recent important changes in emphasis, one in each approach. In classical thermodynamics, much work is being carried out in "moleculeless" continuum mechanical thermostatics. While we seldom use this title, the development of the energy equation explicitly depends upon this approach. In statistical thermodynamics, Tribus' work and that of others dealing with the development of a thermodynamics which relies on information theory alone must be considered as a novel way of developing the same principles one can obtain from "classical" (as opposed to quantum) statistical thermophysics.

Undergraduate chemical engineering thermodynamics courses are apparently so crowded now (too many trees?), that aside from isolated experimental attempts (1) to introduce statistical concepts, only the macroscopic approach is emphasized.

Since we are dealing here only with undergraduate thermodynamics, and since we must recognize that thermodynamics is truly a building block in the over-all concept of chemical engineering process and product design (or if you prefer, systems and materials engineering), the pragmatic philosophy must control the way in which we present the three laws of thermodynamics and their applications to real engineering problems.

Let me point out that, unlike Bates, I believe that the first law of thermodynamics is the "canonical statement" of temperature, the second, of energy, and the third, of entropy. My position, incidentally, places me directly in the path of crossfire from the mechanists who choose work and power for the second and third laws and the thermodynamicists who choose internal energy and reversibility. It is not true, in my opinion that the concept of entropy is more abstract than that of energy, which in turn, is more abstract than that of temperature. All concepts are abstract, if one follows the Platonic philosophy; as a result, if we are to use these concepts in any pragmatic (and hence, engineering) way, we must make approximations to them. The student thinks he knows what temperature is; he makes a "heat" balance and thus has some connection, on paper or by
relation to some physical process such as heat transfer, with the engineer's idea of conservation of energy. However, what makes entropy mysterious (and thus, to the student at least, "more abstract") is not the abstract concept, but our inability to measure it with a meter!

**What Good is Entropy?**

To this question I am tempted to answer "none," at least as entropy is presently taught to undergraduate chemical engineers. If we deal solely with the macroscopic mechanical thermo-statistical developments, the classical development of the concept is through Kelvin refrigerators or Clausius (Carnot) heat engines, via the TS versus PV diagrams, to the second law relating a new variable, called entropy, to a measure of reversible heat and temperature. The next step is to rush into irreversible systems, to "prove" that entropy in any conservative system must either remain constant or increase with time. Siedel (6) at one time collected some 25 statements said to define entropy. At this point, reinforcement of the concept is needed (again because we can't measure entropy) and in desperation and with trepidation, the thermodynamicist dips into statistical thermodynamics and extracts the statement that entropy is a measure of the disorder of the system. Thereby he escapes cross-examination either because the student is too confused to ask for clarification or because no real use is made of the pseudo-concept anyway. Now I wish to raise two questions:

1. Why, if statistical thermodynamics is to be referred to at all, must it be emasculated only to support an archaic approach to the ideas of teaching entropy?

2. Why is it necessary to teach mechanical thermostatics to chemical engineers at all? Carnot engines and Kelvin refrigerators are great devices for making simple heat balances, but certainly more realistic examples like fuel cells, air liquefaction, and fresh water recovery are more vital. The tired answer to this is, of course, that the subject has been presented this way for years, so why rock the boat?

Boat-rocking notwithstanding, I would now propose the pragmatic approach to the concept of entropy, leaning heavily on the recent work of Coleman (4). Rather than 1) wasting time and increasing confusion by introducing statistical thermodynamics and 2) spinning wheels playing with cycles and reversibility-irreversibility, I suggest that the engineer's approximation to the concept of entropy be put to work. From classical thermodynamics we can determine whether a process is reversible or irreversible, but we have no idea of the rate at which a process is approaching an equilibrium state (if ever), or the rate at which conservative (reversible) energy is being converted into dissipative (irreversible) energy. At the risk of sounding like an "Onsagarist," I propose that entropy be used not as a measure of the reversibility of a system, but as a measure of conversion of recoverable energy into nonrecoverable or dissipative energy. Furthermore, that the pragmatic approach to the utilization of entropy be not in the calculation of the conversion from stored energy to energy in motion, but rather in the determination of the time rate of dissipation of energy in the form of heat. This means that we are not restricted to Bates' PV versus TS diagrams, but can now consider interactions between forces and fluxes (in a general way, or if preferred, in the linear Onsagar Law way). Entropy considerations will tell us not only what the system will or will not do but will enable us to obtain a measure of the rate of energy dissipation.

To the student who has suffered through innumerable PV versus TS reversible-irreversible problems and lectures, this "moleculeless continuum mechanical thermodynamics" approach appears as an oasis in a desert of sand and bleached bones of archaic thermodynamicists.

**Conclusion**

If I seem unkind to present approaches to the teaching of thermodynamics, it is because my own experiences as a student are healing very slowly. Thermodynamics, or classical mechanical thermostatics, needs more than first aid. It is dying, and unless non-thermodynamicists recognize the malady as malignant consumption and act quickly, the do-gooders with their adhesive tape will shortly embalm the still-warm body.

I have tried to give an example of an entirely pragmatic approach to a very simple concept, entropy, and, more importantly, an illustration with regard to the direct engineering application of this concept to modern chemical engineering. This approach would almost certainly allow Gibbs to rest quietly — and I doubt that he is resting quietly now.

It is admitted that no mention has been made, either by Bates or me, of chemical thermostatics. For my part, I support the philosophies of Gibbs and Denbigh. Additional comments will be forthcoming.

**REFERENCES**