

close supervision getting familiar with the testing procedures and the handling of the animals. These were done in a closely supervised manner.

After two years' experience, we find the operation of the Center very encouraging. Excellent cooperation has been provided by Natick Laboratories personnel. They have highly praised our students in terms of their working habits as well as their intelligence. The experience was viewed by the students as very valuable.

As the WPI Plan moves into full operation at the upperclass level, project work is expected to consume about half of the total time of the faculty devoted to undergraduate education. The experiences to date in involving chemical engineering students in a wide variety of activities suggest that the transition, though not simple, will be successful. □

CHEMICAL ENGINEERING AT BERKELEY

(Continued from page 10)

Thermodynamics

Experimental and statistical thermodynamic analysis of fluid mixtures. Liquid crystalline behavior and other phase equilibria. Interfacial phenomena. Equations of state based on molecular properties. Electrolyte dissociation and activity-coefficient behavior. Adsorbed state of diatomic molecules. (Bromley, Lyon, Newman, Pigford, Prausnitz, Redlich).

Transport Phenomena

Fluid Mechanics. Laminar-flow systems. Rheology of polymeric systems. Flow of molten alloys. Mechanics of suspended particles. Properties of liquid films. Wave propagation in dispersive media. Mixing and dispersion phenomena in liquids. Drag reduction. (Donaghey, Goren, Newman, Shen, Vermeulen, Wilke, Williams).

Heat Transfer. Nucleate boiling. Promotion of dropwise condensation. Boiling enhancement by additives. Direct-contact heat transfer between immiscible liquids. Thermal conduction of solids. (Bromley, Donaghey, Goren, King, Lyon, Wilke, Williams).

Mass-Transfer Fundamentals. Transport properties of concentrated electrolytes. Absorption with chemical reaction. Atmospheric spread of pollutants. (Grens, Newman, Pigford, Vermeulen).

Separations and Mass Transfer

Gas-liquid mass transfer and accompanying interfacial effects. Computation methods for distillation, extraction, and absorption. Separations of fine-particle systems. Absorption and ion exchange. Oscillatory processes. Foam fractionation. Membrane separations. Separations by freezing. (Goren, Grens, Hanson, King, Klein, Lynn, Merrill, Pigford, Sherwood, Vermeulen, Wilke).

ChE book reviews

Chemical Engineering Thermodynamics: The Study of Energy, Entropy and Equilibrium, R. E. Balzhiser, M. R. Samuels, and J. D. Eliassen, 696 pp. Prentice-Hall, Inc., (1972).

Reviewed by T.S. Storvick, University of Missouri-Columbia

The significant flux of thermodynamics textbooks into the technical literature suggests that there is a general dissatisfaction between authors of these books and those who use them. This book appears to have been conceived in this atmosphere.

The evolution of thermodynamics textbooks indicates that they must now contain the classical material and some new elements:

- It must be written for readers from more than one discipline.
- The particle theory matter must be used in the logical development of the subject.
- The use of electronic computers must be demonstrated.
- Thermodynamics of irreversible processes must be introduced.

The authors have written for Mechanical and Chemical Engineering students (the title is unfortunate in this sense), they have used combinatorial and probability arguments to introduce the entropy function, provided computer codes for several of the calculations in the worked examples and concluded with a short chapter introducing irreversible thermodynamics.

To this reviewer, the relationship that exists between the authors of thermodynamics textbooks and their readers is similar to that of a chef and the clientele of his restaurant. The basic ingredients are always the same but the menu, the division into courses, the spicing and flavoring, and the service and atmosphere are all designed to enhance the practical experience of eating. A satisfactory relationship is established when there is a match between cuisine and palate. It is the same with textbooks.

Most undergraduate engineering students should learn to use classical thermodynamics in their first course on the subject. This book is written for that audience and the authors provide over 90 worked examples and 225 exercises for the student. Some of the exercises will require considerable time to complete. The text is clearly written, the illustrations are generally useful and

there appears to be very few troublesome typographical errors.

The order of presentation is conventional in nearly all respects (except for the introduction of the entropy function discussed below). The thermodynamic functions are introduced in the early chapters, the sections on work producing cycles and fluid flow are expanded to accommodate the needs of the mechanical engineering student. The final 215 pages are devoted to physical and chemical equilibrium of mixtures. A 20 page introduction to the currently important electrochemical processes is also included.

There are some features of the book that may be related to matters of "taste" that this reviewer feels should be discussed in more detail. The mathematical structure of classical thermodynamics is disarmingly simple to undergraduate students who have completed much of their formal work in mathematics. Their concurrent experience with dynamical mechanical systems and the rate processes that are described by more complex mathematical formalism adds to this confusion. The authors never clearly state what experiments establish the relationship of internal energy, volume and composition to the equilibrium state of a system. The mathematical form of the internal energy function as it passes through successive equilibrium states as work is done by the system and heat is added to it is left implicit. This may cause the student more trouble as he seeks to find the relationships between physical systems and the thermodynamic functions.

It is an open question whether statistical thermodynamics should be taught to undergraduate engineering students in their first thermodynamics course. The authors use the mathematics of permutations and combinations to compute the number of distinguishable configurations of a macroscopic thermodynamic system. They then compute the probability p_i that a particular configuration will be found and say, after Boltzmann, that the entropy of that configuration is given by

$$S_i = k \ln p_i.$$

The equilibrium state is then proclaimed to be the one with the maximum probability, $p_{i,\max}$ (and therefore the maximum entropy S_i) consistent with the constraining conditions that there be N particles in volume V with total energy E . None of the statistical thermodynamics formalism is developed and therefore, all of the real compu-

tational power of statistical thermodynamics is lost. The Carnot cycle is used to establish the relationship between reversible heat flow, the thermodynamic temperature and the entropy. It is never clearly established that the total entropy change for all spontaneous processes must be positive and that this is the criteria for all the equilibrium considerations used in later chapters. This presentation does not appear to be a useful way to introduce the entropy function and it cannot be called an introduction to statistical thermodynamics.

One can ask, would it not have been better to use the postulatory approach of Cullen? (*Thermodynamics*, H. B. Cullen, John Wiley, New York, 1960, p. 24-25). This approach establishes the central role of the state function in the mathematical formalism of thermodynamics. It then yields the processes (work and heat flows, mass flows, etc.) by differentiation of the state functions. On page 52, the authors have listed nearly all of the necessary equations to implement this approach. It is still necessary to make the identifications between the mathematical functions and the physical systems that an engineer must make. But, as the authors say, "The utility of the entropy concept depends on relating it to the changes with which we as engineers are involved. Since our concerns are generally macroscopic in nature, it is necessary to associate entropy with macroscopic phenomena, such as heat and work, so that it can be used in the analysis of processes involving these energy flows and interconversions" (page 129). Since the authors follow the phenomenological approach everywhere in their book except for the introduction of the entropy function in Chapter 3, the postulatory approach would be consistent with the presentation they have made. It is also true that the macroscopic descriptions of statistical thermodynamics must be inferred from macroscopic experience whether it is taught before or after a course in applied macroscopic thermodynamics.

There are some specific comments about the presentation that should also be made. The authors have chosen to use the general energy balance for an open system to introduce the relationships between heat and work and the other terms in that balance. The discussion that follows does not establish the important and startling mathematical fact that a conservative or state function, or exact differential of the internal energy written in terms of the physical parame-

ters (for instance, temperature, volume, and composition) is always equal to the heat added to and the work done by the system! Both the heat and work terms are path dependent functions. Once this has been established and is clearly understood by the student, the addition of potential and kinetic energy terms to obtain the general energy balance should cause little difficulty because the students have studied Newtonian mechanics.

The treatment of the entropy function proceeds by writing an entropy balance. It is inferred, but never clearly shown or stated that the entropy is a state function of the same thermodynamic coordinates as the internal energy. The authors use the "lost work" term to account for irreversibilities in a process and therefore do not state the powerful mathematical relationship for all spontaneous processes.

$$\sum_{\text{Subsystems}} \left(\frac{dQ}{T} \right)_{\text{rev}} = dS_{\text{Total}} \geq 0.$$

The authors then write (page 161) "... the third basic equation of thermodynamics (the energy balance and the entropy balance are the other two)"

$$dU_{\text{sys}} = T_{\text{sys}} ds_{\text{sys}} - P_{\text{sys}} dV_{\text{sys}}.$$

This is *not* a third basic equation but rather the combined first and second law equations.

The authors incorrectly state (page 362) that

$$\sum_{i=1}^c n_i d\bar{G}_i = 0$$

is the Gibbs-Duhem equation rather than the previous equation

$$\sum_{i=1}^c n_i d\bar{G}_i = v dP - S dT.$$

The development of the procedures to compute the fugacity coefficient (page 373) does not explicitly state that the integration must proceed on an isotherm (although the original partial derivative that is integrated is clearly marked as taken at constant temperature). Further "... to eliminate computational difficulties in the limit $P^* \rightarrow 0$, we subtract the equation

$$\text{from } \ln(P/P^*) = \int_{P^*}^P \frac{1}{P} dP$$

$$\ln(f/P) = \int_{P^*}^P \frac{V}{RT} dP$$

$$\ln f/P = \int_{P^*}^P \left(\frac{V}{RT} - \frac{1}{P} \right) dP."$$

This is a mathematical problem and the integrand in this final equation still appears to diverge at $P \rightarrow P^* \rightarrow 0$ even with the reassuring statement "we anticipate no further problems arising in the limit $P^* \rightarrow 0$ because the right-hand side remains bounded as P becomes small." This statement could have been made explicit by substituting the compressibility factor $Z/P = V/RT$ and using L'Hopital's rule to obtain

$$\lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P} \right)_T = \frac{B(T)}{RT}$$

where $B(T)$ is the second virial coefficient, a well defined experimental quantity. This procedure not only provides a satisfactory mathematical answer to the problem but provides an analytical method for making the extrapolation.

It is clearly much easier to criticize a book than to write one. The authors have presented their method for presenting thermodynamics to engineering students. They have found this treatment to be successful and this success can only be judged by allowing students to read the book. Their tastes and appetites are nearly always different than those who grew up a decade or two ago.

DEPARTMENT CHAIRMEN

If you have not renewed your departmental subscription to CEE for 1974, please write R. B. Bennett, Business Manager, CEE, Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611.

BULK SUBSCRIPTION RATES: \$4/yr. each, with a \$25.00 minimum for six or fewer subscriptions.

ASEE-CED & AIChE MEMBERS

INDIVIDUAL SUBSCRIPTIONS are available at \$6/yr. (Regular rate \$10/yr.)