BOOKS

Thermodynamics for Engineers, F. H. Crawford and W. D. Van Vorst, Harcourt, Brace & World, Inc., New York (1968), 445 pages, $11.50.

The thermodynamic properties of a system with two degrees of freedom can be defined in many ways. One such possibility is to find one equation of state (for example, the pressure, specific volume, temperature, relationship) and a heat capacity (as a function of pressure and temperature). This method is often used in practice and can be called the *laboratory* approach. **Thermodynamics For Engineers** is almost exclusively (there are a few minor exceptions) concerned with the *laboratory* approach for systems with two variables.

How to compute the entropy of such systems is explained in detail as well as the distinction between natural and unnatural processes. Extremum principles with their applications to the evaluation of equilibrium states are not examined (in the chapter dealing with chemical reactions the mass action law is not derived but postulated). No attempt is made to develop the theory of thermodynamic stability. These limitations reflect the judgment of the authors on what constitutes an introductory thermodynamic course on the junior level. They strive for simplicity since, in their own words, "the difficulties of thermodynamics are usually sufficient without complications".

For the most part they have succeeded in producing a clear and attractive book. This is particularly true of the part dealing with examples and applications which are well chosen, concise, never pedantic, and illuminate the general theory. It is unfortunate that the theory itself is not written with the same exactness. All too often the presentation lacks logic, concepts are ambiguous, and statements misleading. As can be seen from the examples examined below most of these shortcomings could be easily corrected. Since the book is basically sound, it is to be hoped that future editions will be revised accordingly.

1. Diathermic and adiabatic walls are introduced (p. 4) in terms of heat as yet undefined. Similarly, temperature enters (p. 6) in the discussion of thermodynamic equilibrium but is defined later (p. 10).
2. It is stated correctly (p. 6) that "Given enough *time*, temperature differences tend to vanish". On the next page, in apparent contradiction, it is remarked that adiabatic walls prevent thermal equilibrium. Nowhere is it ex-

(Continued on page 685)

(Continued from page 529)

(Continued from page 684)

Thermodynamic equilibrium in the vapor phase esterification of acetic acid with ethanol, Hawes, Russel W., and Robert L. Kabel, **AIChE Journal, 14,** No. 4, p. 606 (July, 1968).

Key Words: A. Equilibrium-8, Chemical Reaction-0, Esterification-9, Ethanol-0, Acetic Acid-0, Etherification-9, Experimental-10, Theoretical-10, Thermal Data-0, Composition-6, Temperature-6, Equilibrium Constant-7.

Abstract: A study of vapor-phase equilibrium in the reaction system, acetic acid-ethanol–ethyl acetate-water, has been made including an evaluation of past investigations, a calculation of equilibrium constants from thermal data, and new experimental determinations utilizing gas chromatography in a novel method. It was found that the magnitude of the thermodynamic equilibrium constant and its true variation with temperature are appreciably different than previously indicated. This is due to the failure of earlier workers to adequately account for competing reactions, primarily the dehydration of ethanol to ethyl ether. Equilibrium constants were obtained at 100, 120.8, and 170°C. for the ethanol dehydration reaction. Equilibrium positions of the esterification reaction have been determined accurately at the same three temperatures, however the corresponding values of the thermodynamic equilibrium constant remain imperfectly specified because of uncertainty concerning the acetic acid association equilibrium.

The steady state behavior of crystallizers with classified product removal, Han, C. D., and Reuel Shinnar, **AIChE Journal, 14,** No. 4, p. 612 (July, 1968).

Key Words: A. Crystallizers-8, 9, Crystallization-8, Classifiers-8, 9, Classifying-6, 8, Steady State-0, Size-7, 8, 9, Distribution-8, Performance-7, Residence Time-6, Mathematical Model-8, Escape-6.

Abstract: This paper deals with the steady state behavior of crystallizers which incorporate some classifying device. A method is described by which the particle size distribution can be calculated for any classifier, provided the crystallizer itself can be considered as a mixed vessel. The method is based on the use of residence time distribution and the escape probability. The effect of classification on crystallizer performance is discussed.

Hydrodynamic stability of marangoni films, Ludviksson, V., and E. N. Lightfoot, **AIChE Journal, 14,** No. 4, p. 620 (July, 1968).

Key Words: A. Stability-7, 8, Marangoni Effect-8, Hydrodynamic-0, Films-9, Liquids-9, Thickness-6, Surface Tension-6, Solids-9, Vertical-0, Heat Transfer-4, Condensers-4, Coolers-4, Columns-4, Electrodes-4, Diffusivity-6.

Abstract: This paper is concerned with the possibility of hydrodynamic instability in a liquid film on a vertical solid surface, formed and maintained against gravity flow by an upward directed, temperature induced surface tension gradient. Analysis in terms of marginal stability shows that all such films are unstable with respect to disturbances of sufficiently long wavelengths. However, it also shows that films tend to be stable for very low and also for very high surface tension gradients. Thicker films tend to be less stable than thin ones and stability decreases with decreasing thermal diffusivity of the liquid.

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(Continued on page 686)

plained that the two notions can be reconciled. Adiabatic walls can maintain a temperature difference only if the observation time is sufficiently short.

3. The authors do not distinguish between a mathematical differential and a small physical change. This is of no importance when each term of a difference equation can be written as a differential by taking the proper limit. Equation 4.14 on the contrary is not proper since Q/dU cannot be defined, dU must be interpreted as a small (but finite) change in U, and the notation, dU, should not be used.

4. The derivation of equation 1.7, and even the writing of functions G_2, G_3 without subscript 1 imply that they are independent of system A (the thermometer). Indeed, G_2, G_3 do not depend on the variables that characterize the state of A, but it is easy to check with examples, that the form of G_2, G_3 depends on the nature of A.

5. To show that the work function, W, is not a state function, it must be shown that W depends on the path that leads to the final state. If W is computed for different final states, represented by the points P', P'', P''' on figure 4.6, the proof becomes meaningless.

6. Because the notions of entropy and reversibility are fundamental, let us finish by some remarks on those questions. It is stated (p. 226) that "the entropy in an isolated system is a monotonically increasing function of time". This is meaningless, since at a given time, before equilibrium is reached, entropy cannot even be defined (in general).

7. Section 8.14 looks at entropy and its statistical interpretation. The "authors try to generalize the notion of entropy by considering it as a phase function which, depending on the phase, can assume different value for the same set of thermodynamical parameters, and try to prove that entropy so derived must increase, with overwhelming probability. However, such a proof has never been given and it is not at all clear how such an artificial generalization of the notion of entropy could be useful to the science of thermodynamics" (see A. I. Khinchin, "Mathematical Foundations of Statistical Mechanics," p. 139).

8. Finally notice that a quasi-static process as defined in section 1.12 is not reversible in general. For instance, consider a cylinder, containing a gas at a pressure p, and a piston. The outside pressure, $\bar{p}$, acting on the piston is constant and much larger than p ($\bar{p}$ could

(Continued on page 688)

be due to a heavy weight put on top of the piston). The piston is maintained in its position by a set of pegs. Remove the pegs and the piston will start moving. Assume that the motion of the piston inside the cylinder is frictionless. We stop the piston almost at once by a second set of pegs placed as close to the first one as desired. We wait until the gas has reached a new state of equilibrium for this new position of the pegs and piston. The new state is as close to the initial state as we want. By repetition of this process we produce a finite change by a succession of equilibrium states (infinite in the limit). Hence we have a quasi-static process which is clearly irreversible. Only if $\bar{p}$ is almost equal to p will the process be reversible, such a process can be called an *equilibrium quasi-static process.* (This counter-example is due to Professor B. T. Chu of Yale University).

Teachers using this textbook should carefully point out these and other weak points to their students to prevent any possible misinterpretation from their part in the fundamental concepts of thermodynamics.

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