CHEMICAL ENGINEERING THERMODYNAMICS

By Thomas E. Daubert
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Reviewed by
T. S. Storvick
University of Missouri-Columbia

When one reads this thermodynamics textbook, the career of the author flashes by. Prof. Daubert spent a major part of his career studying the thermodynamic properties of petroleum fluids. His recent work on the API "Technical Data Book—Petroleum Refining" and the AlChE Design Institute for Physical Properties sponsord "Data Prediction Manual" are widely distributed and well-known. This textbook tends to be a "how to" manual for these major works. The general power of thermodynamic analysis and the elegance of the mathematical structure of classical thermodynamics are reduced by the apparent haste of the author to move on to the details of the calculation of the thermodynamic behavior of petroleum fluids.

The usual chapter headings we expect in a chemical engineering thermodynamics textbook are presented with a different ordering of the material. Starting with a chapter on definitions and p.v.T. properties, Chapters 3 and 4 introduce the first and second laws. Chapter 4 is an example of the ordering of material that the author has chosen. Word statements of the second law are quoted from ten sources followed by the Clausius equality "$\Delta S = dQ_{rev}/T$" [sic] (p. 99). These four pages are followed at once by worked examples calculating numerical values of the change in entropy for ideal and nonideal gas systems, chemical reactions, and lost work process analysis. Then we find Carnot cycle analysis, exergy analysis, the free energy functions and the calculations of the thermodynamic properties (E, H, S, and G) using the ideal gas and real gas equations of state and principle of corresponding states correlations. This chapter ends with analysis of thermal engine cycles and gas liquifaction processes. This is truly an action-packed 90 pages of textbook. From this summary, it appears that the matrix of topics usually covered in a thermo textbook is presented in columns rather than the rows as we have come to expect from other textbooks.

The mathematical relationships among the thermodynamic variables are presented in Chapter 5 using both the Bridgeman tables and Jacobian determinants. Computation and construction of tables and charts is covered in detail (about 30 pages). Chapter 6 presents correlations for estimation of thermodynamic parameters and properties (ρ, mol. wt., T_b, sat. vap. pressure, T_c, p_c, v_c, z_c, ω and mixture combining rules). Chapters 7 and 8 present physical equilibria and the book concludes with a chapter on chemical equilibrium.

Professor Daubert does accomplish his goal of presenting procedures for solving problems of industrial importance. The worked examples and exercises for the student are generally drawn from hydrocarbon processing and substances from fuel conversion processes. The usual fluids, air and water are also used with the number and variety of the problems adequate for a textbook.

The presentation of the structure of thermodynamics is not as well accomplished. Using Chapter 4 again as an example, the first sentence reads, "The essence of thermodynamics is the second law and its applications." That's reassuring to the reader! Three pages later, when introducing the entropy function (4.2 Entropy, pg. 98) one finds the statement, "Entropy is one of the most difficult concepts in thermodynamics for many to grasp as it is intangible and cannot be measured calorimetrically or any other way." This paragraph ends with the statement, "Full proofs and derivations are beyond the scope of this textbook; Denbigh (1981) gives the most lucid analysis." This may be a self-fulfilling prophesy. When an author says the material we're discussing is not easy to explain so why don't you read it elsewhere, the rush to get to the next application may lead to careless statements.

One such statement occurs on page 4 where we find, "*Volume* is the amount of three-dimensional space occupied by a substance and is dependent on the mass of material." Professor Daubert knows that volume is length cubed and has nothing to do with the mass in that volume.

Another hurried definition occurs on page 130. "A *spontaneous process* is simply a process which will occur in some measurable amount of time either in an isolated system or between a system and its surroundings as long as the surroundings have no effect on the process." Given this definition, how does one ac-

Continued on page 38.

TABLE 2
Properties of the
Gamma Residence Time Distribution

Form: $f_T(t) = \frac{1}{\beta^\alpha \Gamma(\alpha)} t^{\alpha-1} \exp\left[-\frac{t}{\beta}\right] \quad \alpha > 0, \beta > 0$

1) $\int_0^\infty f_T(t) = 1$

2) $f_T(t=0) = 0$

3) Mean of the distribution, $\bar{\tau} = \alpha\beta$

4) Variance, $\sigma_T^2 = \alpha\beta^2$

5) $(CV)_T = 1/\sqrt{\alpha}$

6) The j^{th} moment of $f_T(t)$ about the origin:

$$M_T(j) = \frac{\beta^j \Gamma(\alpha + j)}{\Gamma(\alpha)}$$

7) $\psi_T(s) = \frac{1}{(\beta s + 1)^\alpha}$

where s is the Laplace Transform variable for t.

For the special case when $\alpha = 1$, the gamma distribution reduces to an exponential distribution (one well-mixed tank) and β corresponds to the mean residence time in one tank τ.

Figures 1 and 2 depict the shapes of the gamma distribution for different combinations of α and β with the same mean $\alpha\beta$. It can be seen that for a large value of α, the RTD is narrow and corresponds to the plug flow situation illustrating that the plug flow system is nothing but a combination of a large number of small, well-mixed systems. Alternately, the gamma distribution can be interpreted as the sum of independent identical exponential distributions.

NOTATION

$(CV)_T$	coefficient of variation for the RTD
E[x]	expected value of the random variable x
$f_X(x)$	probability density function for the random variable x
g(x)	moment generating function
$M_X(j)$	j^{th} moment about the origin of the probability density function $f_X(x)$
N	number of identical tanks in series
s	Laplace transform variable for t
t	residence time of fluid element in the system
<t>	mean of the residence time distribution

Greek Letters

α	parameter for the gamma residence time distribution
β	parameter for the gamma residence time distribution
$\Gamma(n)$	gamma function
$\Gamma(\alpha,\beta)$	gamma probability density function with parameters α and β
$\psi_x(s)$	Laplace transform of the probability density function $f_X(x)$ with respect to the random variable x
τ	mean residence time

Subscripts

T	residence time distribution

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REVIEW: ChE Thermodynamics

Continued from page 21.

count for thermal energy flow and work done by a spontaneous process: for example, a power plant?

Thermodynamics is an exact mathematical structure based on exact differential forms. The relationship between this structure and the independent variables used to identify the interactions of mass and energy in physical systems and their surroundings requires tight definitions, statements about the systems and the interactions between the system and the surroundings. Professor Daubert has not been very careful with these details in this book.

The solved problems and exercises presented in this book are certainly instructive. The ordering of the material is unconventional but it will probably work in the classroom. Take a careful look at the theoretical development in this book. The application of thermodynamics to a new problem is the test students must pass after completing the thermodynamics course. It is the careful development of these analytical skills that are missing in this book. □