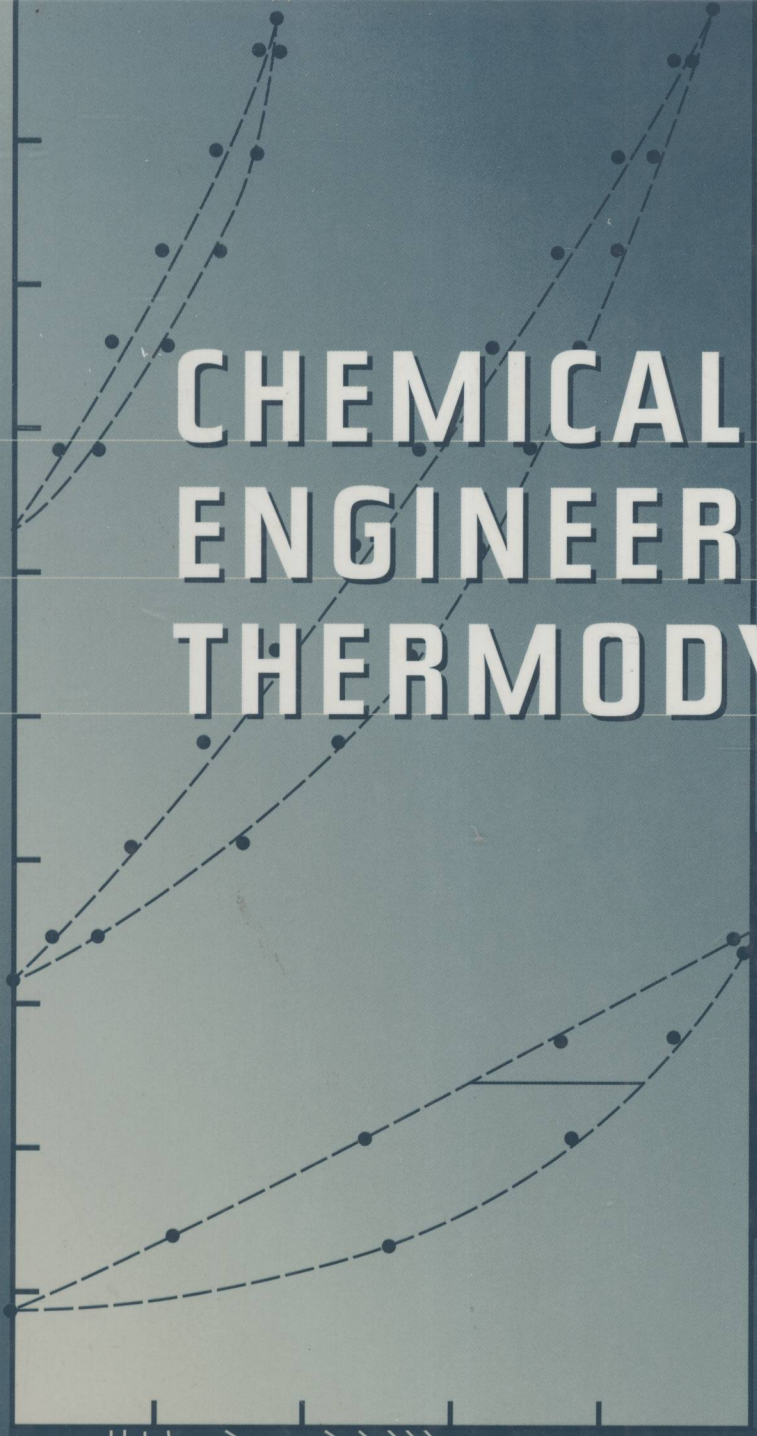
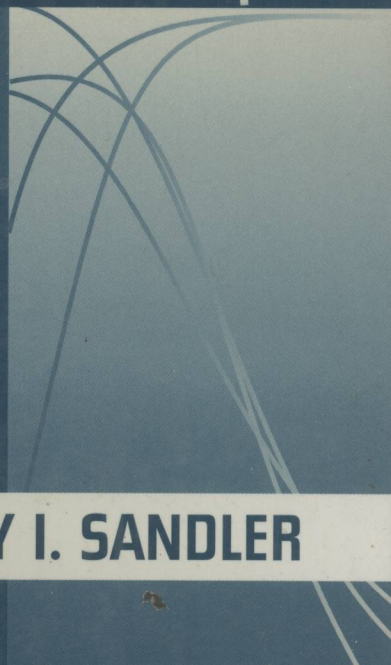
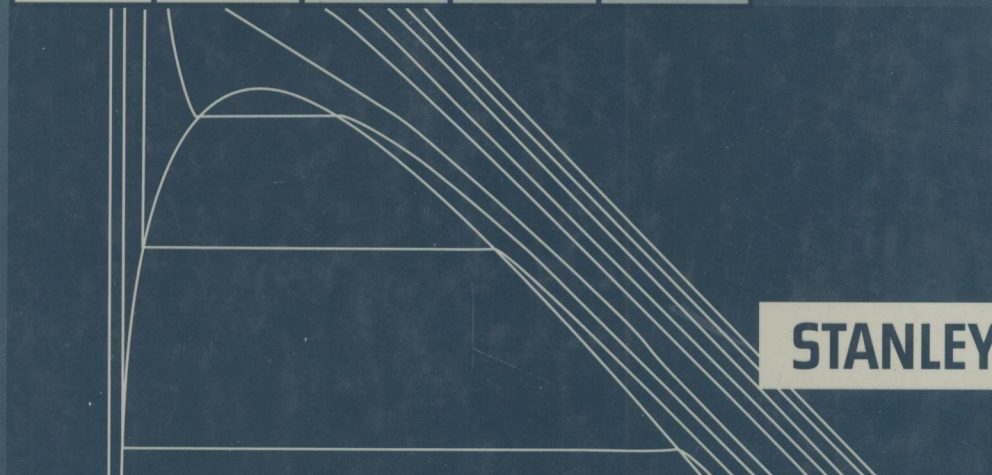
THIRD EDITION

CHEMICAL AND ENGINEERING THERMODYNAMICS







STANLEY I. SANDLER

Chemical and Engineering Thermodynamics

Third Edition

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Chemical and Engineering Thermodynamics

Preface

This book is intended to be the text for a course in thermodynamics for undergraduate students in chemical engineering. It has been used in this manner at the University of Delaware for more than twenty years, originally as a course for third-year students and currently for sophomores. I had two objectives in writing the first edition of this book, which have been retained in the succeeding editions. The first was to develop a modern applied thermodynamics text, especially for chemical engineering students, that was relevant to other parts of the curriculum, specifically courses in separations processes, chemical reactor analysis, and process design. The other objective was to organize and present material in sufficient detail, and in such a way that the student obtained a good understanding of the principles of thermodynamics, and a proficiency in applying these principles to the solution of a large variety of energy flow and equilibrium problems.

Since the first two editions largely met these goals, and the principles of thermodynamics have not changed in the last decade, this edition is similar in structure to the earlier ones. However, there have been three important changes in engineering education in the recent decades. The first is the availability of powerful desktop computers. The second is greater concerns about safety and the environment. The third is the application of chemical engineering principles to new technology areas such as biotechnology, polymers, solid-state processing, etc. In the current edition of this text I have made changes to address each of these issues.

The availability of desktop computers and equation-solving software has now made it possible to bring engineering science, industrial practice, and undergraduate education much closer together. In particular, students in their dormitory rooms or at home can now perform sophisticated thermodynamics and phase equilibrium calculations similar to those that they will encounter in industry. I provide two different ways to accomplish this.

The first is to utilize the set of programs I have developed for certain types of calculations. These programs are for: (1) the calculation of thermodynamic properties and vapor-liquid equilibrium of a pure fluid described by a cubic equation of state; (2) the calculation of the thermodynamic properties and phase equilibria for a multicomponent mixture described by a cubic equation of state; (3) the prediction of activity coefficients in a mixture using the UNIQUAC group contribution activity coefficient model; and (4) the calculation of chemical equilibrium constants and the standard state heats of reaction as a function of temperature using a database of

approximately 100 compounds. These programs are provided both as program code and as stand-alone executable modules.

The second is to make use of computer algebra/calculus programs such as MATHCAD® . The solutions to the illustrations and homework problems in this book were largely done with that program. Alternatively, students and instructors could use similar programs such as MATHEMATICA®, MAPLE®, MATLAB® or others. I believe that such computer algebra programs, that allow students to solve difficult problems without having to become experts in computer programming and numerical analysis, should have an important role throughout the chemical engineering curriculum. Most importantly, they let the student concentrate on the subject matter at hand, here thermodynamics, rather than being distracted by computational methods, algorithms and programming languages. However, while these equation-solving programs are valuable educational tools, there is nothing in this textbook that requires their use. This book can be used with or without such programs as the instructor feels is appropriate. For those who would like to explore the use of such programs, I have prepared a number of problem worksheets using MATHCAD®. The set of programs discussed above and the MATHCAD® worksheets can be downloaded from the Web site for this text. Access *www.wiley.com/college/sandler* and follow the instructions given there.

In an effort to make the subject of thermodynamics more accessible to the student I have made several pedagogical changes in this edition. First, the format of the book has been changed to provide room for marginal notes. The notes I have added are meant to emphasize the concepts I believe to be important, as well as to make it easier for the student to find those concepts again at a later time. Since I frequently write notes in the margins of books, I also wanted to provide a place for students to add notes of their own. A second change was to put boxes around important equations, so that the reader can easily identify the equations that are the end results of sometimes quite detailed analysis. In this way it is hoped that the student will easily see the important tree in what may appear to be a forest of equations. Also, I have provided a short title or description to indicate what is to be learned from or seen in each illustration.

A reader familiar with the second edition of this text will notice that while the basic structure of text is largely unchanged, there are many subtle changes. For example, SI units are now used throughout, and there are many new illustrative and homework problems. Illustrations have been added not only to demonstrate new concepts, but also to provide breaks among pages of mathematical derivations or thermodynamic philosophy. Also, to make thermodynamics and phase equilibria more relevant to the interests of students, I have added several new sections. One section deals with computing the distribution of a chemical pollutant throughout the environment as an illustration of multi-phase equilibria. Two other sections use thermodynamics to understand the dangers of physical and chemical explosions. There are also new sections introducing electrochemical processes, the phase behavior of polymer solutions, the thermodynamic behavior of molten metals, and coupled chemical reactions in biochemical systems. I have also added sections on traditional areas such as the liquefaction of gases, and on power and refrigeration cycles. Finally, I have included a section on the new class of mixing rules that combines equations of state and activity coefficient models. Such mixing rules are perhaps the most important development in applied thermodynamics in the last decade, and have greatly increased the range of applicability and utility of equations of state.

While some of the idiosyncrasies that appeared in the two earlier editions of this text remain here, the reader will find more use of the terms such as the first, second,

and third laws of thermodynamics, and chemical potential than I included in the earlier editions. I prefer, and continue to use, the partial molar Gibbs free energy, which describes the function exactly, to the traditional term of chemical potential. Likewise, I rather use the term energy balance than the first law, etc. Also, I prefer to show that the Carnot efficiency can easily be found once entropy is defined, rather than the more common procedure of introducing entropy (and the second law) in terms of the Carnot cycle. My experience with the latter method is that students have difficulty making the necessary generalization if the concept entropy and the second law are introduced in terms of a specific device.

It has been more than a decade since the appearance of the second edition of this book. During this time many people have encouraged me to prepare this third edition, and have graciously contributed their ideas and advice. The most important contributors have been the undergraduate and graduate students I have taught at Delaware with their incredibly inquisitive minds and penetrating questions. I have also benefited from the helpful comments of faculty colleagues at the University of Delaware and elsewhere who have used the earlier editions of this book. The comments of Professor Raul Lobo (Univ. of Delaware), who taught from a draft version of this third edition, and also contributed several new problems, and Professor Lawrence R. Dodd (Polytechnic Inst. of N.Y.), who has provided many corrections to the earlier edition, are greatly appreciated. Professor Clayton Radke (Univ. California–Berkeley) introduced me to the advantages of using MATHCAD® in undergraduate chemical engineering courses. The use of this tool in this edition is largely the result of the contagion of his enthusiasm that has spread to me. However, again I want to emphasize that there is nothing in this book that requires the use of MATHCAD® or any other equation-solving program.

Perhaps most important in completing this third edition was having the time available to do this. This was provided from several sources. First, and foremost my wife and (now grown) children, who over the years have graciously accepted the fact that I am so inefficient that I always work on evenings and weekends. Judith, my wife, has also proofread the galley proofs and helped prepare the index, and my son Michael has prepared some of the computer programs available on the Web site. Second, from the administration and my faculty colleagues at the University of Delaware who have provided the unencumbered time of a sabbatical leave that proved necessary for the completion of this revision. Finally, I also wish to thank my friends and colleagues in the Departments of Chemical Engineering at the University of California–Berkeley and the University of Queensland (Brisbane, Australia) for their hospitality, companionship and use of their facilities during that sabbatical leave.

Stanley I. Sandler
Newark, Delaware
December 25, 1997

To Judith,
Catherine,
Joel,
And Michael

About the Author

STANLEY I. SANDLER earned the B.Ch.E. degree in 1962 from the City College of New York, and the Ph.D. in chemical engineering from the University of Minnesota in 1966. He was then a National Science Foundation Postdoctoral Fellow at the Institute for Molecular Physics at the University of Maryland for the 1966–67 academic year. He joined the faculty of the University of Delaware in 1967 as an assistant professor, and was promoted to associate professor in 1970, professor in 1973 and Henry Belin du Pont Professor of Chemical Engineering in 1982. He was department chairman from 1982 to 1986. He currently is also professor of chemistry and biochemistry at the University of Delaware and founding director of its Center for Molecular and Engineering Thermodynamics. He has been a visiting professor at Imperial College (London), the Technical University of Berlin, the University of Queensland (Australia) and the University of California, Berkeley.

In addition to this book, Professor Sandler is the author of 225 research papers and a monograph, and he is the editor of a book on thermodynamic modeling and five conference proceedings. Among his many awards and honors are a Faculty Scholar Award (1971) from the Camille and Henry Dreyfus Foundation, a Research Fellowship (1980) and U.S. Senior Scientist Award (1988) from the Alexander von Humboldt Foundation (Germany), the 3M Chemical Engineering Lectureship Award (1988) from the American Society for Engineering Education, the Professional Progress (1984) and Warren K. Lewis Awards (1996) from the American Institute of Chemical Engineers, the E. V. Murphree Award (1996) from the American Chemical Society, the Rossini Lectureship Award (1997) from the International Union of Pure and Applied Chemistry, and election to the U.S. National Academy of Engineering (1996).

Contents

Notation

Standard, generally accepted notation has been used throughout this text. This list contains the important symbols, their definition, and, when appropriate, the page of first occurrence (where a more detailed definition is given). Symbols used only once, or within only a single section are not listed. In a few cases it has been necessary to use the same symbol twice. These occurrences are rare and widely separated, so it is hoped no confusion will result.

SPECIAL NOTATION

Symbol	Designates
$\hat{}$ (caret as in $\hat{H}$)	property per unit mass (enthalpy per unit mass)
$\_$ (underscore as in $\underline{H}$)	property per mole (enthalpy per mole)
$\bar{}$ (overbar as in $\bar{H}_i$)	partial molar property (partial molar enthalpy)
$\pm$ (as in $M_\pm$)	mean ionic property (mean ionic molality)
* (as in G_i^*)	property (Gibbs free energy) in hypothetical pure component state extrapolated from infinite dilution behavior
$\square$ (as in $\bar{G}_i^{\square}$)	ideal unit molal property (Gibbs free energy) extrapolated from infinite dilution behavior
$\circ$	standard state

GENERAL NOTATION

Symbol	Designates
A	Helmholtz free energy (100)
a_i	activity of species i (637)
$a, b, c, \ldots$	constants in heat capacity equation, equation of state, etc.
$B(T), C(T), \ldots$	virial coefficients (197)
$\mathscr{C}$	number of components (324)
°C	degrees Celsius (11)

Symbol	Designates
C_i	concentration of species i (588, 593)
C_V, C_P	constant-volume and constant-pressure heat capacities (44)
C_L	heat capacity at constant length (255)
C_V^*, C_P^*	ideal gas heat capacity (45)
∂, d, D	partial, total, and substantial derivative symbols
D	diffusion coefficient (19)
$\mathcal{F}$	degrees of freedom (304)
°F	degrees Fahrenheit (11)
f	pure component fugacity (280)
$\bar{f}_i$	fugacity of a species in a mixture (391)
F_{fr}	frictional forces (67)
g	acceleration of gravity (8)
G	Gibbs free energy (100)
ΔG^{fus}, ΔG_{rxn}, ΔG_{mix}	Gibbs free energy changes on fusion (576), reaction (351), and mixing (390)
$\Delta G^\circ_{f,i}$	molar Gibbs free energy of formation of species i (350)
H	enthalpy (33)
H_i, $\mathcal{H}_i$	Henry's law constants (448, 449)
ΔH^{vap}, ΔH^{fus}, ΔH^{sub}, ΔH_{mix}, ΔH_{rxn}	enthalpy changes on vaporization (308), fusion (311), sublimation (311), mixing (325), and reaction (350)
$\Delta H^\circ_{C,i}$	standard heat of combustion of species i (352)
$\Delta H^\circ_{f,i}$	molar heat of formation of species i (350)
ΔH_s	molar integral heat solution (380)
I	ionic strength (458) in Chapters 7–9
$\boldsymbol{I}$	unit tensor (82)
K	number of flow streams (27)
K	critical end point (521)
K	degrees Kelvin (11)
K, K_c, K_x	distribution coefficients (495, 587, 588) in Chapter 8
K_a	chemical equilibrium constant (639)
K_c, K_p, K_x, K_y	chemical equilibrium ratios (651) in Chapter 9
K_c°, K_s°	ideal solution ionization (660) and solubility (669) products
k_{fr}	coefficient of sliding friction (68)
K_i	K-factor, y_i/x_i (494)
K_s	solubility product (668)
K_γ	product of activity coefficients (652)
K_ν	product of fugacity coefficients (652)
K_{OW}	octanol-water position coefficient (593)

L	moles of liquid phase (493)
L	lower critical end point (521)
M	mass (8)
$\dot{M}$	mass flow rate (27)
m	molecular weight (27)
$\mathcal{M}$	number of independent chemical reactions (340)
ΔM_k	amount of mass that entered from kth flow stream (28)
M_1	mass of system in state 1 (28) or mass of species 1 (342)
M	melting point (521)
N	number of moles (27)
$N_{i,0}$	initial number of moles of species i (340)
P	pressure (9)
$\boldsymbol{P}$	pressure tensor (80)
$\mathcal{P}$	number of phases (303)
P^{vap}, P^{sub}, P^{sat}	vapor (308), sublimation (308), and saturation pressures (308)
P_{atm}	atmospheric pressure (9)
P_C, $P_{C,m}$	critical pressure (226) and mixture pseudocritical pressure (439)
P_T	triple point pressure (277)
P_g	gauge pressure (8)
P_i	partial pressure of species i (480)
P_r, $P_{r,m}$	reduced pressure for a pure component (229) and a mixture (439)
P_{rxn}	reaction pressure (647)
Q, $\dot{Q}$	heat flow (19) and heat flow rate (30)
$\mathbf{q}$	heat flux vector (80)
q	volumetric flow rate (691)
R	gas constant (10)
r	specific reaction rate (340)
S	entropy (91)
S_{gen}, $\dot{S}_{gen}$	entropy generated (93) and entropy generation rate (91)
S_{UV}, S_{UN}, etc.	second partial derivatives of entropy (266)
T	temperature (10)
T_C, $T_{C,m}$	critical temperature (226) and mixture pseudocritical temperature (439)
T_f	mixture freezing temperature (598)
T_{lc}, T_{uc}	lower and upper consolute temperatures (557)
T_m	melting temperature (575)
T_r, $T_{r,m}$	reduced temperature of a pure fluid (229) and a mixture (439)
T_T	triple point temperature (277, 577)
U	internal energy and mixture internal energy (324)
V	volume (10), mixture volume (324) (also moles of vapor in Secs. 8.1 and 9.4 only)

Symbol	Designates
ΔV^{fus}	volume change on melting or fusion (578)
v	velocity (20)
v_{S}	velocity of sound (255)
$\mathbf{v}$	velocity vector (80)
V_C	molar critical volume (226)
ΔV_{mix}	volume change on mixing (325)
V_r	reduced volume (229)
w_i	mass fraction (325)
W, $\dot{W}$	work (31) and rate at which work is supplied to system (31)
W^{NET}	net work supplied from surroundings (70)
W_{fr}	work against function (70)
W_s, $\dot{W}_s$	shaft work (30) and rate of shaft work (30)
X	any thermodynamic variable in Chapter 4, molar extent of chemical reaction (337) elsewhere
x	coordinate direction
x^{I}, x^{II}	fraction of mass in a phase (50)
x^{L}, x^{V}	fraction of mass in vapor and liquid phases (274)
x_{i}	mole fraction of species i in vapor or liquid phase (325)
Y	any thermodynamic variable (176)
y	coordinate direction
y_i	vapor-phase mole fraction (406)
Z, Z_m	compressibility factor of a pure fluid (197) and a mixture (435)
z	coordinate direction
Z_C	critical compressibility (227)
z_+, z_-	ionic valence (456)
α	coefficient of thermal expansion (179) (in Chapter 4)
α, β	coefficients in van Laar and Debye-Hückel equations (Chapters 7–9)
γ	specific heat ratio (65)
γ_{i}, γ_{i}^{*}, $\gamma_{\text{i}}^{\square}$	activity coefficients of species i (399, 448, 449)
$\gamma_{\pm}$	mean ionic activity coefficient (457)
δ	solubility parameter (431)
δ_{ij}	Kronecker delta function (164)
θ	general thermodynamic variable (26, 50)
κ_{S}	adiabatic compressibility (251)
κ_{T}	isothermal compressibility (179)
μ	viscosity (20), Joule-Thomson coefficient (185), chemical potential (367)
ν	stoichiometric coefficient (337)
ν_+, ν_-	ionic stoichiometric coefficient (456)