CHEMICAL
ENGINEERING
SERIES

INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS

Fifth Edition

J. M. Smith
Professor Emeritus of Chemical Engineering
University of California, Davis

H. C. Van Ness
Institute Professor Emeritus of Chemical Engineering
Rensselaer Polytechnic Institute

M. M. Abbott
Professor of Chemical Engineering
Rensselaer Polytechnic Institute

The McGraw-Hill Companies, Inc.

New York St. Louis San Francisco Auckland Bogotá Caracas Lisbon
London Madrid Mexico City Milan Montreal New Delhi
San Juan Singapore Sydney Tokyo Toronto

McGraw-Hill

A Division of The McGraw-Hill Companies

INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS

This book is printed on acid-free paper.

6 7 8 9 0 DOC DOC 9 0 9

ISBN 0-07-059239-X

This book was set in Computer Modern Roman by Publication Services, Inc.
The editors were B. J. Clark, Kiran Kimbell, and John M. Morriss;
the production supervisor was Annette Mayeski.
The cover was designed by Joan Greenfield.
Project supervision was done by Publication Services, Inc.
R. R. Donnelley & Sons Company was printer and binder.

Library of Congress Catalog Card Number: 95-81742

INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS

McGraw-Hill Chemical Engineering Series

Building the Literature of a Profession

Fifteen prominent chemical engineers first met in New York more than 60 years ago to plan a continuing literature for their rapidly growing profession. From industry came such pioneer practitioners as Leo H. Baekeland, Arthur D. Little, Charles L. Reese, John V. N. Dorr, M. C. Whitaker, and R. S. McBride. From the universities came such eminent educators as William H. Walker, Alfred H. White, D. D. Jackson, J. H. James, Warren K. Lewis, and Harry A. Curtis. H. C. Parmelee, then editor of *Chemical and Metallurgical Engineering,* served as chairman and was joined subsequently by S. D. Kirkpatrick as consulting editor.

After several meetings, this committee submitted its report to the McGraw-Hill Book Company in September 1925. In the report were detailed specifications for a correlated series of more than a dozen texts and reference books which have since become the McGraw-Hill Series in Chemical Engineering and which became the cornerstone of the chemical engineering curriculum.

From this beginning there has evolved a series of texts surpassing by far the scope and longevity envisioned by the founding Editorial Board. The McGraw-Hill Series in Chemical Engineering stands as a unique historical record of the development of chemical engineering education and practice. In the series one finds the milestones of the subject's evolution: industrial chemistry, stoichiometry, unit operations and processes, thermodynamics, kinetics, and transfer operations.

Chemical engineering is a dynamic profession, and its literature continues to evolve. McGraw-Hill, with its editor, B.J. Clark and its consulting editors, remains committed to a publishing policy that will serve, and indeed lead, the needs of the chemical engineering profession during the years to come.

The Series

Bailey and Ollis: *Biochemical Engineering Fundamentals*
Bennett and Myers: *Momentum, Heat, and Mass Transfer*
Brodkey and Hershey: *Transport Phenomena: A Unified Approach*
Carberry: *Chemical and Catalytic Reaction Engineering*
Constantinides: *Applied Numerical Methods with Personal Computers*
Coughanowr: *Process Systems Analysis and Control*
de Nevers: *Air Pollution Control Engineering*
de Nevers: *Fluid Mechanics for Chemical Engineers*
Douglas: *Conceptual Design of Chemical Processes*
Edgar and Himmelblau: *Optimization of Chemical Processes*
Gates, Katzer, and Schuit: *Chemistry of Catalytic Processes*
Green: *Perry's Chemical Engineers' Handbook*
Holland: *Fundamentals of Multicomponent Distillation*
Katz and Lee: *Natural Gas Engineering: Production and Storage*
King: *Separation Processes*
Lee: *Fundamentals of Microelectronics Processing*
Luyben: *Process Modeling, Simulation, and Control for Chemical Engineers*
McCabe, Smith, and Harriott: *Unit Operations of Chemical Engineering*
Marlin: *Process Control: Designing Processes and Control Systems for Dynamic Performance*
Middleman and Hochberg: *Process Engineering Analysis in Semiconductor Device Fabrication*
Perry and Chilton (Editors): *Perry's Chemical Engineers' Handbook*
Peters and Timmerhaus: *Plant Design and Economics for Chemical Engineers*
Reid, Prausnitz, and Poling: *Properties of Gases and Liquids*
Smith, Van Ness, and Abbott: *Introduction to Chemical Engineering Thermodynamics*
Treybal: *Mass Transfer Operations*
Valle-Riestra: *Project Evaluation in the Chemical Process Industries*
Wentz: *Hazardous Waste Management*

LIST OF SYMBOLS

A	Area
A	Helmholtz energy
A	Parameter in Eq. (4.4)
a	Acceleration
a	Molar area of an adsorbed phase
a	Parameter in cubic equations of state
a_i	Activity of pure species i
$\bar{a}_i$	Partial parameter, cubic equations of state
$\hat{a}_i$	Activity of species i in solution
B	Second virial coefficient, density expansion
B	Parameter in Eq. (4.4)
B'	Second virial coefficient, pressure expansion
B^0, B^1	Functions in generalized second-virial-coefficient correlation
B_{ij}	Interaction second virial coefficient
b	Parameter in cubic equations of state
$\bar{b}_i$	Partial parameter, cubic equations of state
C	Third virial coefficient, density expansion
C	Parameter in Eq. (4.4)
C'	Third virial coefficient, pressure expansion
C_{ijk}	Interaction third virial coefficient
C_P	Molar or specific heat capacity at constant pressure
C_V	Molar or specific heat capacity at constant volume
C_P^E	Excess heat capacity at constant pressure
C_P°	Standard-state heat capacity at constant pressure
ΔC_P°	Standard heat-capacity change of reaction
$\langle C_P \rangle_H$	Mean heat capacity for enthalpy calculations
$\langle C_P \rangle_S$	Mean heat capacity for entropy calculations
$\langle C_P^\circ \rangle_H$	Mean standard heat capacity for enthalpy calculations
$\langle C_P^\circ \rangle_S$	Mean standard heat capacity for entropy calculations
c	Speed of sound
D	Fourth virial coefficient, density expansion
D	Parameter in Eq. (4.4)

D'	Fourth virial coefficient, pressure expansion
E_i	Energy level
E_K	Kinetic energy
E_P	Gravitational potential energy
F	Degrees of freedom (phase rule)
F	Force
f_i	Fugacity of pure species i
f_i°	Standard-sate fugacity
$\hat{f}_i$	Fugacity of species i in solution
G	Molar or specific Gibbs energy $\equiv H - TS$
G_i°	Standard-state Gibbs energy of species i
$\bar{G}_i$	Partial Gibbs energy of species i in solution
G^E	Excess Gibbs energy $\equiv G - G^{id}$
G^R	Residual Gibbs energy $\equiv G - G^{ig}$
ΔG	Gibbs energy change of mixing
ΔG°	Standard Gibbs-energy change of reaction
ΔG_f°	Standard Gibbs-energy change of formation
g	Local acceleration of gravity
g_c	Dimensional constant $= 32.1740(\mathrm{lb_m})(\mathrm{ft})(\mathrm{lb_f})^{-1}(\mathrm{s})^{-2}$
g_i	Degeneracy
H	Molar or specific enthalpy $\equiv U + PV$
$\bar{H}_i$	Partial enthalpy of species i in solution
H^E	Excess enthalpy $\equiv H - H^{id}$
H^R	Residual enthalpy $\equiv H - H^{ig}$
$(H^R)^0$, $(H^R)^1$	Functions in generalized residual-enthalpy correlation
ΔH	Enthalpy change ("heat") of mixing
$\widetilde{\Delta H}$	Heat of solution
ΔH°	Standard enthalpy change of reaction
ΔH_0°	Standard heat of reaction at reference temperature T_0
ΔH_f°	Standard enthalpy change of formation
h	Planck's constant
I	First ionization potential
K_j	Equilibrium constant for chemical reaction j
K_i	Vapor/liquid equilibrium constant for species i
k	Boltzmann's constant
k_i	Henry's constant for species i in solution
k_{ij}	Equation-of-state interaction parameter
$\mathcal{L}$	Molar fraction of system that is liquid
$\mathbf{M}$	Mach number
M	Molar mass (molecular weight)
M	Molar or specific value of extensive thermodynamic property
$\bar{M}_i$	Partial property of species i in solution
M^E	Excess property $\equiv M - M^{id}$
M^R	Residual property $\equiv M - M^{ig}$

ΔM	Property change of mixing
ΔM°	Standard property change of reaction
ΔM_f°	Standard property change of formation
m	Mass
$\dot{m}$	Mass flow rate
N	Number of chemical species (phase rule)
N_A	Avogadro's number
n	Number of moles
$\tilde{n}$	Moles of solvent per mole of solute
n_i	Number of moles of species i
P	Absolute pressure
P°	Pressure in the standard state
P_c	Critical pressure
P_r	Reduced pressure
P_0	Reference pressure
p_i	Partial pressure of species i
P_i^{sat}	Saturation vapor pressure of species i
Q	Heat
$\dot{Q}$	Rate of heat transfer
q	Electric charge
R	Universal gas constant
r	Intermolecular separation
r	Number of independent chemical reactions (phase rule)
S	Molar or specific entropy
$\bar{S}_i$	Partial entropy of species i in solution
S^E	Excess entropy $\equiv S - S^{id}$
S^R	Residual entropy $\equiv S - S^{ig}$
$(S^R)^0$, $(S^R)^1$	Functions in generalized residual entropy correlation
$\dot{S}_G$	Rate of entropy generation in control volume
$S_{G,\text{total}}$	Total entropy generation per unit amount of fluid
$\dot{S}_{G,\text{total}}$	Total rate of entropy generation
ΔS	Entropy change of mixing
ΔS°	Standard entropy change of reaction
ΔS_f°	Standard entropy change of formation
T	Absolute temperature in kelvins or rankines
T_c	Critical temperature
T_n	Normal-boiling-point temperature
T_r	Reduced temperature
T_0	Reference temperature
T_σ	Absolute temperature of surroundings
T_i^{sat}	Saturation temperature of species i
t	Temperature in °C or (°F)
U	Molar or specific internal energy
$\mathcal{U}$	Intermolecular pair-potential function

u	Velocity
V	Molar or specific volume
$\mathcal{V}$	Molar fraction of system that is vapor
$\bar{V}_i$	Partial volume of species i in solution
V_c	Critical volume
V_r	Reduced volume
V^E	Excess volume $\equiv V - V^{id}$
V^R	Residual volume $\equiv V - V^{ig}$
ΔV	Volume change of mixing
W	Work
$\dot{W}$	Work rate (power)
W_{ideal}	Ideal work
$\dot{W}_{\text{ideal}}$	Ideal work rate
W_{lost}	Lost work
$\dot{W}_{\text{lost}}$	Lost work rate
W_s	Shaft work for flow process
$\dot{W}_s$	Shaft power for flow process
x_i	Mole fraction of species i in general or in a liquid phase
x^v	Quality
y_i	Mole fraction of species i in a vapor phase
Z	Compressibility factor $\equiv PV/RT$
Z_c	Critical compressibility factor $\equiv P_cV_c/RT_c$
Z^0, Z^1	Functions in generalized compressibility-factor correlation
$\mathcal{Z}$	Partition function
z	Adsorbed phase compressibility factor; defined by Eq. (14.48)
z	Elevation above a datum level
z_i	Overall mole fraction or mole fraction in a solid phase

Superscripts

E	Denotes excess thermodynamic property
av	Denotes phase transition from adsorbed phase to vapor
id	Denotes value for an ideal solution
ig	Denotes value for an ideal gas
l	Denotes liquid phase
lv	Denotes phase transition from liquid to vapor
R	Denotes residual thermodynamic property
s	Denotes solid phase
sl	Denotes phase transition from solid to liquid
t	Denotes a total value of an extensive thermodynamic property
v	Denotes vapor phase
∞	Denotes a value at infinite dilution

Subscripts

C	Denotes a value for a cold heat reservoir
c	Denotes a value for the critical state
cv	Denotes a control volume
fs	Denotes flowing streams
H	Denotes a value for a hot heat reservoir
r	Denotes a reduced value

Greek letters

α	Polarizability
α,β	As superscripts, identify phases
β	Volume expansivity
Γ_i	Integration constant
γ	Ratio of heat capacities C_P/C_V
γ_i	Activity coefficient of species i in solution
ϵ	Well depth in intermolecular potential function
ϵ_0	Electric permittivity of vacuum
ε	Reaction coordinate
η	Efficiency
κ	Isothermal compressibility
Π	Spreading pressure in adsorbed phase
π	Number of phases (phase rule)
μ	Dipole moment
μ_i	Chemical potential of species i
ν_i	Stoichiometric number of species i
ρ	Molar density
ρ_c	Critical density
ρ_r	Reduced density
σ	Molecular collision diameter
τ	Time
τ	Temperature ratio $\equiv T/T_0$ [$\equiv 1 - T_r$ in Eq. (6.56)]
Φ_i	Ratio of fugacity coefficients, defined by Eq. (12.2)
ϕ_i	Fugacity coefficient of pure species i
$\hat{\phi}_i$	Fugacity coefficient of species i in solution
ϕ^0, ϕ^1	Functions in generalized fugacity-coefficient correlation
ω	Acentric factor

Notes

$^\circ$	As a superscript, denotes the standard state
$\bar{}$	Overbar denotes a partial property
$\dot{}$	Overdot denotes a time rate
$\hat{}$	Circumflex denotes a property in solution
Δ	Difference operator

PREFACE

The purpose of this text is to present thermodynamics from a chemical engineering viewpoint. The laws of thermodynamics are universal, but are most effectively taught in the context of the discipline of student commitment. This is the justification for a separate text for chemical engineers, just as it has been for the previous four editions, which have been in print for 47 years.

In writing this text, we have sought to maintain the rigor characteristic of sound thermodynamic analysis, while at the same time providing a treatment that may be readily understood by the average undergraduate. The material includes much that is of an introductory nature, but the development is carried far enough to allow application to significant problems in chemical-engineering practice. Indeed, the content is more than adequate for an academic-year undergraduate course, and is sufficiently comprehensive to make the book a useful reference both in graduate courses and for professional practice.

For a student new to this subject a demanding task of discovery lies ahead. New ideas, terms, and symbols appear at a bewildering rate. The challenge, ever present, is to think topics through to the point of understanding, to acquire the capacity to reason, and to apply this fundamental body of knowledge to the solution of practical problems. Moreover, knowledge gained here is enlarged and refined as the educational experience continues.

The first two chapters of the book present basic definitions and a development of the first law as it applies to nonflow and simple steady-flow processes. Chapters 3 and 4 treat the pressure/volume/temperature behavior of fluids and certain heat effects, allowing early application of the first law to important engineering problems. The second law and some of its applications are considered in Chap. 5. A treatment of the thermodynamic properties of pure fluids in Chap. 6 leads to application in Chap. 7 of the first and second laws to flow processes in general and in Chaps. 8 and 9 to power production and refrigeration processes. The remainder of the book, dealing with fluid mixtures, treats topics in the unique domain of chemical-engineering thermodynamics. Chapters 10 and 11 provide a comprehensive exposition of the thermodynamic properties of fluid mixtures, and of their

uses in vapor/liquid equilibrium and in mixing processes. Chapter 12 is devoted to a detailed treatment of vapor/liquid equilibrium for systems at modest pressures. The application of equations of state in thermodynamic calculations, particularly in vapor/liquid equilibrium, is discussed in Chap. 13, and additional topics related to phase equilibria are treated in Chap. 14. Chemical-reaction equilibrium is covered at length in Chap. 15. Finally, Chap. 16 deals with the thermodynamic analysis of real processes, affording a review of much of the practical subject matter of thermodynamics.

We gratefully acknowledge the contributions of Professor Charles Muckenfuss, Debra L. Sauke, and Eugene N. Dorsi, whose efforts produced computer programs for calculation of the thermodynamic properties of steam and ultimately the steam tables of Appendix F. We thank those who offered detailed and constructive criticism of the fourth edition: Philip T. Eubank, Texas A&M University; Dana E. Knox, New Jersey Institute of Technology; Joseph C. Mullins, Clemson University, and Bruce E. Poling, University of Toledo. With respect to the present edition, we appreciate the efforts of Alan L. Myers, University of Pennsylvania, and Keith E. Gubbins, Cornell University, who reviewed parts of the manuscript, and of John J. Hwalek, University of Maine, who contributed expert advice regarding the Mathcad® solutions of Appendix D.

J. M. Smith
H. C. Van Ness
M. M. Abbott

Contents