



McGraw-Hill's

CHEMICAL ENGINEERING SERIES

# Introduction to Chemical Engineering Thermodynamics

SEVENTH EDITION

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

---

# INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS

---

SEVENTH 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*



**Higher Education**

Boston Burr Ridge, IL Dubuque, IA Madison, WI New York San Francisco St. Louis  
Bangkok Bogotá Caracas Kuala Lumpur Lisbon London Madrid Mexico City  
Milan Montreal New Delhi Santiago Seoul Singapore Sydney Taipei Toronto

The McGraw-Hill Companies



**Higher Education**

## INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS, SEVENTH EDITION

Published by McGraw-Hill, a business unit of The McGraw-Hill Companies, Inc., 1221 Avenue of the Americas, New York, NY 10020. Copyright " 2005, 2001, 1996, 1987, 1975, 1959, 1949 by The McGraw-Hill Companies, Inc. All rights reserved. No part of this publication may be reproduced or distributed in any form or by any means, or stored in a database or retrieval system, without the prior written consent of The McGraw-Hill Companies, Inc., including, but not limited to, in any network or other electronic storage or transmission, or broadcast for distance learning.

Some ancillaries, including electronic and print components, may not be available to customers outside the United States.

This book is printed on acid-free paper.

1 2 3 4 5 6 7 8 9 0 DOC/DOC 0 9 8 7 6 5 4

ISBN 0-07-310445-0

Publisher: *Elizabeth A. Jones*  
Senior Sponsoring Editor: *Suzanne Jeans*  
Developmental Editor: *Kathleen L. White*  
Senior Marketing Manager: *Mary K. Kittell*  
Project Coordinator: *Melissa M. Leick*  
Senior Production Supervisor: *Laura Fuller*  
Media Technology Producer: *Eric A. Weber*  
Designer: *Laurie B. Janssen*  
Compositor: *Lachina Publishing Services*  
Typeface: *10/12 Times Roman*  
Printer: *R. R. Donnelley Crawfordsville, IN*

### Library of Congress Cataloging-in-Publication Data

Smith, J. M. (Joe Mauk)

Introduction to chemical engineering thermodynamics. — 7th ed. / J.M. Smith, Hendrick C. Van Ness,  
Michael M. Abbott.

p. cm. — (McGraw-Hill series in civil and environmental engineering)

Includes index.

ISBN 0-07-310445-0 (acid-free paper)

1. Thermodynamics. 2. Chemical engineering. I. Title: Chemical engineering thermodynamics. II. Van Ness, H. C. (Hendrick C.). III. Abbott, Michael M. IV. Title. V. Series.

TP155.2.T45S58 2005  
660'.2969—dc22

2004058781  
CIP

www.mhhe.com

# List of Symbols

$A$	Area
$A$	Molar or specific Helmholtz energy $\equiv U - TS$
$A$	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.76), Eq. (12.14)
$a$	Acceleration
$a$	Molar area, adsorbed phase
$a$	Parameter, cubic equations of state
$\bar{a}_i$	Partial parameter, cubic equations of state
$B$	Second virial coefficient, density expansion
$B$	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.76), Eq. (12.14)
$\hat{B}$	Reduced second-virial coefficient, defined by Eq. (3.62)
$B'$	Second virial coefficient, pressure expansion
$B^0, B^1$	Functions, generalized second-virial-coefficient correlation
$B_{ij}$	Interaction second virial coefficient
$b$	Parameter, cubic equations of state
$\bar{b}_i$	Partial parameter, cubic equations of state
$C$	Third virial coefficient, density expansion
$C$	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.76), Eq. (12.14)
$\hat{C}$	Reduced third-virial coefficient, defined on p. 103
$C'$	Third virial coefficient, pressure expansion
$C^0, C^1$	Functions, generalized third-virial-coefficient correlation
$C_P$	Molar or specific heat capacity, constant pressure
$C_V$	Molar or specific heat capacity, constant volume
$C_P^\circ$	Standard-state heat capacity, constant pressure
$\Delta C_P^\circ$	Standard heat-capacity change of reaction
$\langle C_P \rangle_H$	Mean heat capacity, enthalpy calculations
$\langle C_P \rangle_S$	Mean heat capacity, entropy calculations
$\langle C_P^\circ \rangle_H$	Mean standard heat capacity, enthalpy calculations
$\langle C_P^\circ \rangle_S$	Mean standard heat capacity, entropy calculations
$c$	Speed of sound
$D$	Fourth virial coefficient, density expansion
$D$	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.77)
$D'$	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
$\mathcal{F}$	Faraday's constant
$f_i$	Fugacity, pure species $i$
$f_i^\circ$	Standard-state fugacity
$\hat{f}_i$	Fugacity, species $i$ in solution
$G$	Molar or specific Gibbs energy $\equiv H - TS$
$G_i^\circ$	Standard-state Gibbs energy, species $i$
$\bar{G}_i$	Partial Gibbs energy, species $i$ in solution
$G^E$	Excess Gibbs energy $\equiv G - G^{id}$
$G^R$	Residual Gibbs energy $\equiv G - G^{ig}$
$\Delta G$	Gibbs-energy change of mixing
$\Delta G^\circ$	Standard Gibbs-energy change of reaction
$\Delta G_f^\circ$	Standard Gibbs-energy change of formation
$g$	Local acceleration of gravity
$g_c$	Dimensional constant $= 32.1740(\text{lb}_m)(\text{ft})(\text{lb}_f)^{-1}(\text{s})^{-2}$
$g_i$	Degeneracy
$H$	Molar or specific enthalpy $\equiv U + PV$
$\mathcal{H}_i$	Henry's constant, species $i$ in solution
$H_i^\circ$	Standard-state enthalpy, pure species $i$
$\bar{H}_i$	Partial enthalpy, 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, generalized residual-enthalpy correlation
$\Delta H$	Enthalpy change ("heat") of mixing; also, latent heat of phase transition
$\widetilde{\Delta H}$	Heat of solution
$\Delta H^\circ$	Standard enthalpy change of reaction
$\Delta H_0^\circ$	Standard heat of reaction at reference temperature $T_0$
$\Delta H_f^\circ$	Standard enthalpy change of formation
$h$	Planck's constant
$I$	Represents an integral, defined, e.g., by Eqs. (6.65)
$I$	First ionization potential
$K_j$	Equilibrium constant, chemical reaction $j$
$K_i$	Vapor/liquid equilibrium ratio, species $i \equiv y_i/x_i$
$k$	Boltzmann's constant
$\mathcal{L}$	Molar fraction of system that is liquid
$l$	Length
$l_{ij}$	Equation-of-state interaction parameter, Eq. (14.101)
<b>M</b>	Mach number
$M$	Molar mass (molecular weight)
$M$	Molar or specific value, extensive thermodynamic property
$\bar{M}_i$	Partial property, species $i$ in solution
$M^E$	Excess property $\equiv M - M^{id}$
$M^R$	Residual property $\equiv M - M^{ig}$
$\Delta M$	Property change of mixing

$\Delta M^\circ$	Standard property change of reaction
$\Delta M_f^\circ$	Standard property change of formation
$m$	Mass
$\dot{m}$	Mass flowrate
$N$	Number of chemical species, phase rule
$N_A$	Avogadro's number
$n$	Number of moles
$\dot{n}$	Molar flowrate
$\tilde{n}$	Moles of solvent per mole of solute
$n_i$	Number of moles, species $i$
$P$	Absolute pressure
$P^\circ$	Standard-state pressure
$P_c$	Critical pressure
$P_r$	Reduced pressure
$P_r^0, P_r^1$	Functions, generalized vapor-pressure correlation
$P_0$	Reference pressure
$p_i$	Partial pressure, species $i$
$P_i^{\text{sat}}$	Saturation vapor pressure, species $i$
$Q$	Heat
$\dot{Q}$	Rate of heat transfer
$q$	Volumetric flowrate
$q$	Parameter, cubic equations of state
$q$	Electric charge
$\bar{q}_i$	Partial parameter, cubic equations of state
$R$	Universal gas constant (Table A.2)
$r$	Compression ratio
$r$	Intermolecular separation
$r$	Number of independent chemical reactions, phase rule
$S$	Molar or specific entropy
$\bar{S}_i$	Partial entropy, 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, generalized residual-entropy correlation
$S_G$	Entropy generation per unit amount of fluid
$\dot{S}_G$	Rate of entropy generation
$\Delta S$	Entropy change of mixing
$\Delta S^\circ$	Standard entropy change of reaction
$\Delta S_f^\circ$	Standard entropy change of formation
$T$	Absolute temperature, kelvins or rankines
$T_c$	Critical temperature
$T_n$	Normal-boiling-point temperature
$T_r$	Reduced temperature
$T_0$	Reference temperature
$T_\sigma$	Absolute temperature of surroundings
$T_i^{\text{sat}}$	Saturation temperature, species $i$

$t$	Temperature, °C or (°F)
$t$	Time
$U$	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, species $i$ in solution
$V_c$	Critical volume
$V_r$	Reduced volume
$V^E$	Excess volume $\equiv V - V^{id}$
$V^R$	Residual volume $\equiv V - V^{ig}$
$\Delta V$	Volume change of mixing; also, volume change of phase transition
$W$	Work
$\dot{W}$	Work rate (power)
$W_{\text{ideal}}$	Ideal work
$\dot{W}_{\text{ideal}}$	Ideal-work rate
$W_{\text{lost}}$	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, species $i$ , liquid phase or general
$x^v$	Quality
$y_i$	Mole fraction, species $i$ , vapor phase
$Z$	Compressibility factor $\equiv PV/RT$
$Z_c$	Critical compressibility factor $\equiv P_c V_c / RT_c$
$Z^0, Z^1$	Functions, generalized compressibility-factor correlation
$\mathcal{Z}$	Partition function
$z$	Adsorbed phase compressibility factor, defined by Eq. (14.108)
$z$	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
$\infty$	Denotes a value at infinite dilution

*Greek letters*

$\alpha$	Function, cubic equations of state (Table 3.1, p. 98)
$\alpha$	Polarizability
$\alpha, \beta$	As superscripts, identify phases
$\alpha\beta$	As superscript, denotes phase transition from phase $\alpha$ to phase $\beta$
$\beta$	Volume expansivity
$\beta$	Parameter, cubic equations of state
$\Gamma_i$	Integration constant
$\gamma$	Ratio of heat capacities $C_P/C_V$
$\gamma_i$	Activity coefficient, species $i$ in solution
$\delta$	Polytropic exponent
$\epsilon$	Constant, cubic equations of state
$\epsilon$	Well depth, intermolecular potential function
$\epsilon_0$	Electric permittivity of vacuum
$\varepsilon$	Reaction coordinate
$\eta$	Efficiency
$\kappa$	Isothermal compressibility
$\Pi$	Spreading pressure, adsorbed phase
$\Pi$	Osmotic pressure
$\pi$	Number of phases, phase rule
$\mu$	Joule/Thomson coefficient
$\mu$	Dipole moment
$\mu_i$	Chemical potential, species $i$
$\nu_i$	Stoichiometric number, species $i$
$\rho$	Molar or specific density $\equiv 1/V$
$\rho_c$	Critical density
$\rho_r$	Reduced density
$\sigma$	Constant, cubic equations of state
$\sigma$	Molecular collision diameter
$\tau$	Temperature ratio $\equiv T/T_0$ [In Eq. (6.77), $\tau \equiv 1 - T_r$ ]
$\Phi_i$	Ratio of fugacity coefficients, defined by Eq. (14.2)
$\phi_i$	Fugacity coefficient, pure species $i$
$\hat{\phi}_i$	Fugacity coefficient, species $i$ in solution
$\phi^0, \phi^1$	Functions, generalized fugacity-coefficient correlation
$\Psi, \Omega$	Constants, cubic equations of state
$\omega$	Acentric factor

*Notes*

cv	As a subscript, denotes a control volume
fs	As a subscript, denotes flowing streams
o	As a superscript, denotes the standard state
–	Overbar denotes a partial property
•	Overdot denotes a time rate
^	Circumflex denotes a property in solution
$\Delta$	Difference operator



# Preface

Thermodynamics, one of the central subjects of science, is based on laws of universal applicability. The justification for presenting the subject from a chemical-engineering viewpoint is our conviction that it is most effectively taught in the context of the discipline of student commitment.

Although *introductory* in nature, the material of this text should not be thought simple. Indeed, there is no way to make it simple, and a student new to the subject will find that a demanding task of discovery lies ahead. New concepts, words, and symbols appear at a bewildering rate, and here memory plays a part. A far greater challenge is the necessity to develop a capacity to reason and to apply thermodynamic principles in the solution of practical problems. While maintaining the rigor characteristic of sound thermodynamic analysis, we have made every effort to avoid unnecessary mathematical complexity. Moreover, we encourage understanding by writing simple active-voice, present-tense sentences. We can hardly supply the required motivation, but our objective, as it has been for all previous editions, is a treatment that may be understood by any student willing to exercise due diligence.

The first two chapters of the book present basic definitions and a development of the first law. Chapters 3 and 4 treat the pressure/volume/temperature behavior of fluids and certain heat effects, allowing early application of the first law to realistic 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 allows general application of the first and second laws, and provides for an expanded treatment of flow processes in Chap. 7. Chapters 8 and 9 deal with power production and refrigeration processes. The remainder of the book, concerned with fluid mixtures, treats topics in the unique domain of chemical-engineering thermodynamics. Chapters 11 and 12 provide a comprehensive exposition of the theory and application of solution thermodynamics. Chemical-reaction equilibrium is covered at length in Chap. 13. Chapter 14 deals with topics in phase equilibria, including an extended treatment of vapor/liquid equilibrium, and adsorption and osmotic equilibria. Chapter 15 treats the thermodynamic analysis of real processes, affording a review of much of the practical subject matter of thermodynamics.

The material of these 15 chapters is more than adequate for an academic-year undergraduate course, and discretion, conditioned by the content of other courses, is required in the choice of what is covered. The first 13 chapters include material thought necessary as part of any chemical engineer's education. Where only a single-semester course in chemical-engineering thermodynamics is provided, these 13 chapters may represent sufficient content.

The laws and principles of classical thermodynamics do not depend on any particular model of the structure of matter; they are free of any molecular considerations. However, the behavior exhibited by matter—gases, liquids, and solids—does depend on its particulate nature, and in Chapter 16 we present an introduction to molecular thermodynamics, to which reference is occasionally made in earlier chapters.

The book is comprehensive enough to make it a useful reference both in graduate courses and for professional practice. However, length considerations make necessary a prudent selectivity. Thus, we do not include certain topics worthy of attention, but of a specialized nature. These include applications to polymers, electrolytes, and biomaterials.

We are indebted to many individuals—students, professors, reviewers—who have contributed in various ways to the quality of this seventh edition, directly and indirectly, through question and comment, praise and criticism, over the 55 years and six editions of its evolution. To all we extend our thanks.

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

# Contents

List of Symbols	xi
Preface	xvii
<b>1 INTRODUCTION</b>	<b>1</b>
1.1 The Scope of Thermodynamics	1
1.2 Dimensions and Units	2
1.3 Measures of Amount or Size	2
1.4 Force	3
1.5 Temperature	5
1.6 Pressure	6
1.7 Work	8
1.8 Energy	10
1.9 Heat	15
<b>2 THE FIRST LAW AND OTHER BASIC CONCEPTS</b>	<b>21</b>
2.1 Joule's Experiments	21
2.2 Internal Energy	21
2.3 The First Law of Thermodynamics	22
2.4 Energy Balance for Closed Systems	23
2.5 Thermodynamic State and State Functions	26
2.6 Equilibrium	29
2.7 The Phase Rule	29
2.8 The Reversible Process	31
2.9 Constant- $V$ and Constant- $P$ Processes	37
2.10 Enthalpy	38
2.11 Heat Capacity	40
2.12 Mass and Energy Balances for Open Systems	44
<b>3 VOLUMETRIC PROPERTIES OF PURE FLUIDS</b>	<b>64</b>
3.1 $PVT$ Behavior of Pure Substances	64
3.2 Virial Equations of State	70
3.3 The Ideal Gas	73
3.4 Application of the Virial Equations	87
3.5 Cubic Equations of State	90
3.6 Generalized Correlations for Gases	99
3.7 Generalized Correlations for Liquids	109

<b>4</b>	<b>HEAT EFFECTS</b>	<b>125</b>
4.1	Sensible Heat Effects	125
4.2	Latent Heats of Pure Substances	133
4.3	Standard Heat of Reaction	135
4.4	Standard Heat of Formation	136
4.5	Standard Heat of Combustion	139
4.6	Temperature Dependence of $\Delta H^\circ$	140
4.7	Heat Effects of Industrial Reactions	143
<b>5</b>	<b>THE SECOND LAW OF THERMODYNAMICS</b>	<b>159</b>
5.1	Statements of the Second Law	160
5.2	Heat Engines	161
5.3	Thermodynamic Temperature Scales	163
5.4	Entropy	167
5.5	Entropy Changes of an Ideal Gas	170
5.6	Mathematical Statement of the Second Law	173
5.7	Entropy Balance for Open Systems	176
5.8	Calculation of Ideal Work	181
5.9	Lost Work	185
5.10	The Third Law of Thermodynamics	188
5.11	Entropy from the Microscopic Viewpoint	188
<b>6</b>	<b>THERMODYNAMIC PROPERTIES OF FLUIDS</b>	<b>199</b>
6.1	Property Relations for Homogeneous Phases	199
6.2	Residual Properties	208
6.3	Residual Properties by Equations of State	215
6.4	Two-Phase Systems	220
6.5	Thermodynamic Diagrams	225
6.6	Tables of Thermodynamic Properties	226
6.7	Generalized Property Correlations for Gases	230
<b>7</b>	<b>APPLICATIONS OF THERMODYNAMICS TO FLOW PROCESSES</b>	<b>254</b>
7.1	Duct Flow of Compressible Fluids	255
7.2	Turbines (Expanders)	268
7.3	Compression Processes	273
<b>8</b>	<b>PRODUCTION OF POWER FROM HEAT</b>	<b>290</b>
8.1	The Steam Power Plant	291
8.2	Internal-Combustion Engines	302
8.3	Jet Engines; Rocket Engines	310
<b>9</b>	<b>REFRIGERATION AND LIQUEFACTION</b>	<b>317</b>
9.1	The Carnot Refrigerator	317
9.2	The Vapor-Compression Cycle	318
9.3	The Choice of Refrigerant	321
9.4	Absorption Refrigeration	323
9.5	The Heat Pump	326
9.6	Liquefaction Processes	327

<b>10</b>	<b>VAPOR/LIQUID EQUILIBRIUM: INTRODUCTION</b>	<b>338</b>
10.1	The Nature of Equilibrium	338
10.2	The Phase Rule, Duhem's Theorem	339
10.3	VLE: Qualitative Behavior	341
10.4	Simple Models for Vapor/Liquid Equilibrium	347
10.5	VLE by Modified Raoult's Law	358
10.6	VLE from $K$ -Value Correlations	363
<b>11</b>	<b>SOLUTION THERMODYNAMICS: THEORY</b>	<b>378</b>
11.1	Fundamental Property Relation	378
11.2	The Chemical Potential and Phase Equilibria	380
11.3	Partial Properties	381
11.4	The Ideal-Gas Mixture Model	391
11.5	Fugacity and Fugacity Coefficient: Pure Species	394
11.6	Fugacity and Fugacity Coefficient: Species in Solution	401
11.7	Generalized Correlations for the Fugacity Coefficient	407
11.8	The Ideal-Solution Model	411
11.9	Excess Properties	413
<b>12</b>	<b>SOLUTION THERMODYNAMICS: APPLICATIONS</b>	<b>430</b>
12.1	Liquid-Phase Properties from VLE Data	430
12.2	Models for the Excess Gibbs Energy	446
12.3	Property Changes of Mixing	449
12.4	Heat Effects of Mixing Processes	456
<b>13</b>	<b>CHEMICAL-REACTION EQUILIBRIA</b>	<b>483</b>
13.1	The Reaction Coordinate	484
13.2	Application of Equilibrium Criteria to Chemical Reactions	488
13.3	The Standard Gibbs-Energy Change and the Equilibrium Constant	489
13.4	Effect of Temperature on the Equilibrium Constant	492
13.5	Evaluation of Equilibrium Constants	496
13.6	Relation of Equilibrium Constants to Composition	498
13.7	Equilibrium Conversions for Single Reactions	502
13.8	Phase Rule and Duhem's Theorem for Reacting Systems	514
13.9	Multireaction Equilibria	518
13.10	Fuel Cells	529
<b>14</b>	<b>TOPICS IN PHASE EQUILIBRIA</b>	<b>545</b>
14.1	The Gamma/Phi Formulation of VLE	545
14.2	VLE from Cubic Equations of State	556
14.3	Equilibrium and Stability	575
14.4	Liquid/Liquid Equilibrium (LLE)	581
14.5	Vapor/Liquid/Liquid Equilibrium (VLLE)	590
14.6	Solid/Liquid Equilibrium (SLE)	597
14.7	Solid/Vapor Equilibrium (SVE)	602
14.8	Equilibrium Adsorption of Gases on Solids	606
14.9	Osmotic Equilibrium and Osmotic Pressure	621

<b>15</b>	<b>THERMODYNAMIC ANALYSIS OF PROCESSES</b>	<b>635</b>
15.1	Thermodynamic Analysis of Steady-State Flow Processes .....	635
<b>16</b>	<b>INTRODUCTION TO MOLECULAR THERMODYNAMICS</b>	<b>647</b>
16.1	Molecular Theory of Fluids.....	647
16.2	Second Virial Coefficients from Potential Functions.....	654
16.3	Internal Energy of Ideal Gases: Microscopic View .....	657
16.4	Thermodynamic Properties and Statistical Mechanics .....	660
16.5	Hydrogen Bonding and Charge-Transfer Complexing .....	662
16.6	Behavior of Excess Properties .....	665
16.7	Molecular Basis for Mixture Behavior.....	669
16.8	VLE by Molecular Simulation .....	672
<b>A</b>	<b>Conversion Factors and Values of the Gas Constant</b>	<b>677</b>
<b>B</b>	<b>Properties of Pure Species</b>	<b>679</b>
<b>C</b>	<b>Heat Capacities and Property Changes of Formation</b>	<b>683</b>
<b>D</b>	<b>Representative Computer Programs</b>	<b>688</b>
D.1	Defined Functions .....	688
D.2	Solution of Example Problems by Mathcad® .....	691
<b>E</b>	<b>The Lee/Kesler Generalized-correlation Tables</b>	<b>695</b>
<b>F</b>	<b>Steam Tables</b>	<b>712</b>
F.1	Interpolation .....	712
<b>G</b>	<b>Thermodynamic Diagrams</b>	<b>788</b>
<b>H</b>	<b>UNIFAC Method</b>	<b>791</b>
<b>I</b>	<b>Newton's Method</b>	<b>798</b>
	<b>Name Index</b>	<b>803</b>
	<b>Subject Index</b>	<b>807</b>

# Chapter 1

---

## Introduction

### 1.1 THE SCOPE OF THERMODYNAMICS

The science of thermodynamics was born in the nineteenth century of the need to describe the operation of steam engines and to set forth the limits of what they can accomplish. Thus the name itself denotes power developed from heat, with obvious application to heat engines, of which the steam engine was the initial example. However, the principles observed to be valid for engines are readily generalized, and are known as the first and second laws of thermodynamics. These laws have no proof in the mathematical sense; their validity lies in the absence of contrary experience. Thus thermodynamics shares with mechanics and electromagnetism a basis in primitive laws.

These laws lead through mathematical deduction to a network of equations which find application in all branches of science and engineering. The chemical engineer copes with a particularly wide variety of problems. Among them are calculation of heat and work requirements for physical and chemical processes, and the determination of equilibrium conditions for chemical reactions and for the transfer of chemical species between phases.

Thermodynamic considerations do not establish the *rates* of chemical or physical processes. Rates depend on driving force and resistance. Although driving forces are thermodynamic variables, resistances are not. Neither can thermodynamics, a macroscopic-property formulation, reveal the microscopic (molecular) mechanisms of physical or chemical processes. On the other hand, knowledge of the microscopic behavior of matter can be useful in the calculation of thermodynamic properties.<sup>1</sup> Property values are essential to the practical application of thermodynamics. The chemical engineer deals with many chemical species, and experimental data are often lacking. This has led to development of “generalized correlations” that provide property estimates in the absence of data.

The application of thermodynamics to any real problem starts with the identification of a particular body of matter as the focus of attention. This body of matter is called the *system*, and its thermodynamic state is defined by a few measurable macroscopic properties. These depend on the fundamental *dimensions* of science, of which length, time, mass, temperature, and amount of substance are of interest here.

<sup>1</sup> An elementary treatment is presented in Chap. 16.

## 1.2 DIMENSIONS AND UNITS

The *fundamental* dimensions are *primitives*, recognized through our sensory perceptions and not definable in terms of anything simpler. Their use, however, requires the definition of arbitrary scales of measure, divided into specific *units* of size. Primary units have been set by international agreement, and are codified as the International System of Units (abbreviated SI, for *Système International*).

The *second*, symbol s, the SI unit of time, is the duration of 9,192,631,770 cycles of radiation associated with a specified transition of the cesium atom. The *meter*, symbol m, is the fundamental unit of length, defined as the distance light travels in a vacuum during  $1/299,792,458$  of a second. The *kilogram*, symbol kg, is the mass of a platinum/iridium cylinder kept at the International Bureau of Weights and Measures at Sèvres, France. The unit of temperature is the *kelvin*, symbol K, equal to  $1/273.16$  of the thermodynamic temperature of the triple point of water. A detailed discussion of temperature, the characteristic dimension of thermodynamics, is given in Sec. 1.5. The *mole*, symbol mol, is defined as the amount of substance represented by as many elementary entities (e.g., molecules) as there are atoms in 0.012 kg of carbon-12. This is equivalent to the “gram mole” commonly used by chemists.

Multiples and decimal fractions of SI units are designated by prefixes. Those in common use are listed in Table 1.1. Thus, the centimeter is given as  $1\text{ cm} = 10^{-2}\text{ m}$ , and the kilogram as  $1\text{ kg} = 10^3\text{ g}$ .

**Table 1.1: Prefixes for SI Units**

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
$10^{-15}$	femto	f	$10^2$	hecto	h
$10^{-12}$	pico	p	$10^3$	kilo	k
$10^{-9}$	nano	n	$10^6$	mega	M
$10^{-6}$	micro	$\mu$	$10^9$	giga	G
$10^{-3}$	milli	m	$10^{12}$	tera	T
$10^{-2}$	centi	c	$10^{15}$	peta	P

Other systems of units, such as the English engineering system, use units that are related to SI units by fixed conversion factors. Thus, the foot (ft) is defined as 0.3048 m, the pound mass ( $\text{lb}_m$ ) as 0.45359237 kg, and the pound mole ( $\text{lb mol}$ ) as 453.59237 mol.

## 1.3 MEASURES OF AMOUNT OR SIZE

Three measures of amount or size are in common use:

- Mass,  $m$
- Number of moles,  $n$
- Total volume,  $V^t$

These measures for a specific system are in direct proportion to one another. Mass, a *primitive* without definition, may be divided by the molar mass  $M$ , commonly called the molecular



weight, to yield number of moles:

$$n = \frac{m}{M} \quad \text{or} \quad m = Mn$$

Total volume, representing the size of a system, is a defined quantity given as the product of three lengths. It may be divided by the mass or number of moles of the system to yield *specific* or *molar volume*:

- Specific volume:  $V \equiv \frac{V^t}{m} \quad \text{or} \quad V^t = mV$
- Molar volume:  $V \equiv \frac{V^t}{n} \quad \text{or} \quad V^t = nV$

Specific or molar density is defined as the reciprocal of specific or molar volume:  $\rho \equiv V^{-1}$ .

These quantities ( $V$  and  $\rho$ ) are independent of the size of a system, and are examples of *intensive* thermodynamic variables. They are functions of the temperature, pressure, and composition of a system, additional quantities that are independent of system size.

## 1.4 FORCE

The SI unit of force is the *newton*, symbol N, derived from Newton's second law, which expresses force  $F$  as the product of mass  $m$  and acceleration  $a$ ; thus  $F = ma$ . The newton is defined as the force which when applied to a mass of 1 kg produces an acceleration of  $1 \text{ m s}^{-2}$ ; thus the newton is a *derived* unit representing  $1 \text{ kg m s}^{-2}$ .

In the English engineering system of units, force is treated as an additional independent dimension along with length, time, and mass. The pound *force* ( $\text{lb}_f$ ) is defined as that force which accelerates 1 pound *mass* 32.1740 feet per second per second. Newton's law must here include a dimensional proportionality constant for consistency with this definition:

$$F = \frac{1}{g_c} ma$$

Whence,<sup>2</sup> 
$$1(\text{lb}_f) = \frac{1}{g_c} \times 1(\text{lb}_m) \times 32.1740(\text{ft})(\text{s})^{-2}$$

and 
$$g_c = 32.1740(\text{lb}_m)(\text{ft})(\text{lb}_f)^{-1}(\text{s})^{-2}$$

The pound *force* is equivalent to 4.4482216 N.

Because force and mass are different concepts, a pound *force* and a pound *mass* are different quantities, and their units do not cancel one another. When an equation contains both units, ( $\text{lb}_f$ ) and ( $\text{lb}_m$ ), the dimensional constant  $g_c$  must also appear in the equation to make it dimensionally correct.

<sup>2</sup>Where non-SI units (e.g., English units) are employed, parentheses enclose the abbreviations of all units.