

FUNDAMENTALS F Thermodynamics

Sixth Edition

FUNDAMENTALS OF THERMODYNAMICS

SIXTH EDITION

RICHARD E. SONNTAG CLAUS BORGNAKKE

University of Michigan

GORDON J. VAN WYLEN

Hope College (emeritus)



Acquisitions Editor Production Editor Marketing Manager Senior Designer

Production Management Services

Cover Photo

Joseph Hayton Sandra Russell Katherine Hepburn

Dawn L. Stanley

UG / GGS Information Services, Inc. © Judy Dole/The Image Bank

This book was typeset in 10/12 Times New Roman By UG / GGS Information Services, Inc. and printed and bound by R. R. Donnelley and Sons (Willard). The cover was printed by Phoenix Color Corp.

The paper in this book was manufactured by a mill whose forest management programs include sustained yield harvesting of its timberlands. Sustained yield harvesting principles ensure that the number of trees cut each year does not exceed the amount of new growth.

This book is printed on acid-free paper.



Copyright © 2003 by John Wiley & Sons, Inc. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc. 111 River Street, Hoboken, NJ 07030, (201) 748-6008, E-mail: PERMREQ@WILEY.COM. To order books or for customer service call 1-800-CALL-WILEY (225-5945).

Richard E. Sonntag, Claus Borgnakke, and Gordon J. Van Wylen Fundamentals of Thermodynamics, sixth edition

ISBN 0-471-15232-3

Printed in the United States of America.

10 9 8 7 6 5 4 3 2

Fundamental Physical Constants

Avogadro	$N_0 = 6.022 \ 136 \times 10^{23} \ l/mol$
Boltzmann	$k = 1.380 658 \times 10^{-23} \text{ J/K}$
Planck	$h = 6.626 076 \times 10^{-34} \text{ Js}$
Gas Constant	$\bar{R} = N_0 k = 8.314 51 \text{ J/mol K}$
Atomic Mass Unit	$m_0 = 1.660 540 \times 10^{-27} \mathrm{kg}$
Velocity of light	$c = 2.997 925 \times 10^8 \text{ m/s}$
Electron Charge	$e = 1.602 177 \times 10^{-19} C$
Electron Mass	$m_e = 9.109389 \times 10^{-31} \mathrm{kg}$
Proton Mass	$m_p = 1.672 623 \times 10^{-27} \text{ kg}$
Gravitation (Std.)	$g = 9.80665 \text{ m/s}^2$
Stefan Boltzmann	$\sigma = 5.670 51 \times 10^{-8} \text{W/m}^2 \text{K}^4$

Prefixes

10^{-1}	deci	d
10^{-2}	centi	С
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{1}	deka	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P

Concentration

 10^{-6} parts per million ppm

FUNDAMENTALS OF THERMODYNAMICS

SIXTH EDITION

PREFACE

In this sixth edition we have retained the basic objective of the earlier editions:

- to present a comprehensive and rigorous treatment of classical thermodynamics while retaining an engineering perspective, and in doing so
- to lay the groundwork for subsequent studies in such fields as fluid mechanics, heat transfer, and statistical thermodynamics, and also
- to prepare the student to effectively use thermodynamics in the practice of engineering.

We have deliberately directed our presentation to students. New concepts and definitions are presented in the context where they are first relevant in a natural progression. The first thermodynamic properties to be defined (Chapter 2) are those that can be readily measured: pressure, specific volume, and temperature. In Chapter 3, tables of thermodynamic properties are introduced, but only in regard to these measurable properties. Internal energy and enthalpy are introduced in connection with the first law, entropy with the second law, and the Helmholtz and Gibbs functions in the chapter on thermodynamic relations. Many real world realistic examples have been included in the book to assist the student in gaining an understanding of thermodynamics, and the problems at the end of each chapter have been carefully sequenced to correlate with the subject matter and are grouped and identified as such. The early chapters in particular contain a much larger number of examples, illustrations, and problems than in previous editions, and throughout the book, chapter-end summaries are included, followed by a set of concept/study problems that should be of benefit to the students.

NEW FEATURES IN THIS EDITION

End-of-Chapter Summaries

The new end-of-chapter summaries provide a short review of the main concepts covered in the chapter, with highlighted key words. To further enhance the summary we have listed the set of skills that the student should have mastered after studying the chapter. These skills are among the outcomes that can be tested with the accompanying set of study-guide problems in addition to the main set of homework problems.

Main Concepts and Formulas

Main concepts and formulas are included at the end of each chapter for reference.

Study Guide Problems

We have made a set of study guide problems for each chapter as a quick check of the chapter material. These are selected to be short and directed toward a very specific concept. A student can answer all of these questions to assess their level of understanding, and determine if any of the subjects need to be studied further. These problems are also suitable to use together with the rest of the homework problems in assignments and included in the solution manual.

Homework Problems

The number of homework problems has been greatly expanded and now exceeds 2,400. A large number of introductory problems have been added to cover all aspects of the chapter material. We have furthermore separated the problems into sections according to subject for easy selection according to the particular coverage given. A number of more comprehensive problems have been retained and grouped in the end as review problems.

Tables

The tables of the substances have been expanded to include the specific internal energy in the superheated vapor region. The ideal gas tables have been printed on a mass basis as well as a mole basis, to reflect their use on mass basis early in the text, and mole basis for the combustion and chemical equilibrium chapters.

Revisions

In this edition we have incorporated a number of developments and approaches included in our recent textbook, Introduction to Engineering Thermodynamics, Richard E. Sonntag and Claus Borgnakke, John Wiley & Sons, Inc. (2001). In Chapter 3, we first introduce thermodynamic tables, and then note the behavior of superheated vapor at progressively lower densities, which leads to the definition of the ideal gas model, then the compressibility factor and equations of state. In Chapter 5, the result of ideal gas energy depending only on temperature follows the examination of steam table values at different temperatures and pressures. Second law presentation in Chapter 7 is streamlined, with better integration of the concepts of thermodynamic temperature and ideal gas temperature. Coverage of ideal gas and ideal gas mixtures focuses on unit mass basis, instead of mole basis, and is simpler. Development of availability and reversible work in Chapter 10 focuses on the steady-state process, and leads to the general expression for exergy. We have therefore included a new section on the general exergy balance to amplify the concept of transport and destruction of exergy. The chapter with property relations is slightly reorganized and streamlined to also focus on properties on a mass basis. Due to current technology developments we have expanded our discussion of the fuel cells and also updated the chapter with combustion.

Expanded Software Included

In this edition we have included the expanded software CATT2 that includes a number of additional substances besides those included in the printed tables in Appendix B. A number of hydrocarbon fuels, refrigerants, and cryogenic fluids are included and a

printed version is available in the booklet Thermodynamic and Transport Properties, Claus Borgnakke and Richard E. Sonntag, John Wiley & Sons, Inc. (1997).

FLEXIBILITY IN COVERAGE AND SCOPE

We have attempted to cover fairly comprehensively the basic subject matter of classical thermodynamics, and believe that the book provides adequate preparation for study of the application of thermodynamics to the various professional fields as well as for study of more advanced topics in thermodynamics, such as those related to materials, surface phenomena, plasmas, and cryogenics. We also recognize that a number of colleges offer a single introductory course in thermodynamics for all departments, and we have tried to cover those topics that the various departments might wish to have included in such a course. However, since specific courses vary considerably in prerequisites, specific objectives, duration, and background of the students, we have arranged the material, particularly in the later chapters, so that there is considerable flexibility in the amount of material that may be covered.

Units

Our philosophy regarding units in this edition has been to organize the book so that the course or sequence can be taught entirely in SI units (Le Système International d'Unités). Thus, all the text examples are in SI units, as are the complete problem sets and the thermodynamic tables. In recognition, however, of the continuing need for engineering graduates to be familiar with English Engineering units, we have included an introduction to this system in Chapter 2. We have also repeated a sufficient number of examples, problems, and tables in these units, which should allow for suitable practice for those who wish to use these units. For dealing with English units, the force-mass conversion question between pound mass and pound force is treated simply as a units conversion, without using an explicit conversion constant. Throughout, symbols, units and sign conventions are treated as in previous editions.

Supplements and Additional Support

Additional support is made available through a companion website at www.wiley.com/ college/sonntag. Tutorials and reviews of all the basic material as indicated in the main text by the ThermoNet icon are accessible through the companion website. The website allows students to go through a self-paced study developing the basic skill set associated with the various subjects usually covered in a first course in thermodynamics.

The chapter on compressible flow is also available at www.wiley.com/college/ sonntag and revised with summary, study guide problems, and new homework problems. We recognize that in many cases this chapter is not included in the thermodynamics courses, but may instead be covered elsewhere in the curriculum.

We have tried to include material appropriate and sufficient for a two-semester course sequence, and to provide flexibility for choice of topic coverage. Instructors may want to visit the companion website at www.wiley.com/college/sonntag for information and suggestions on possible course structure and schedules, additional study problem material, and current errata for the book.

ACKNOWLEDGMENTS

We acknowledge with appreciation the suggestions, counsel, and encouragement of many colleagues, both at the University of Michigan and elsewhere. This assistance has been very helpful to us during the writing of this edition, as it was with the earlier editions of the book. Both undergraduate and graduate students have been of particular assistance, for their perceptive questions have often caused us to rewrite or rethink a given portion of the text, or to try to develop a better way of presenting the material in order to anticipate such questions or difficulties. Finally, for each of us, the encouragement and patience of our wives and families have been indispensable and have made this time of writing pleasant and enjoyable, in spite of the pressures of the project. A special thanks to a number of colleagues at other institutions, who have reviewed the book and provided input to the revisions. Some of the reviewers are

Edward E. Anderson, Texas Tech University Haim H. Bau, University of Pennsylvania Pei-Feng Hsu, Florida Institute of Technology Gerald J. Micklow, University of Alabama Jayathi Y. Murthy, Carnegie Mellon University Anthony J. Wheeler, San Francisco State University

We also wish to thank our editor, Joseph Hayton, for his effort in the planning and the support and encouragement during the production of this edition.

Our hope is that this book will contribute to the effective teaching of thermodynamics to students who face very significant challenges and opportunities during their professional careers. Your comments, criticism, and suggestions will also be appreciated and you may channel that through Claus Borgnakke, claus@umich.edu.

> RICHARD E. SONNTAG CLAUS BORGNAKKE GORDON J. VAN WYLEN Ann Arbor, Michigan April 2002

SYMBOLS

```
acceleration
a
A
          area
          specific Helmholtz function and total Helmholtz function
a, A
AF
          air-fuel ratio
B_{\varsigma}
          adiabatic bulk modulus
          isothermal bulk modulus
B_T
C
          velocity of sound
          mass fraction
C
          coefficient of discharge
C_D
C_p
          constant-pressure specific heat
          constant-volume specific heat
          zero-pressure constant-pressure specific heat
          zero-pressure constant-volume specific heat
          specific energy and total energy
e, E
F
           force
FA
          fuel-air ratio
           acceleration due to gravity
g
           specific Gibbs function and total Gibbs function
g, G
           specific enthalpy and total enthalpy
h, H
           electrical current
i
           irreversibility
           proportionality factor to relate units of work to units of heat
J
           specific heat ratio: C_p/C_v
k
           equilibrium constant
K
           kinetic energy
KE
           length
L
           mass
m
           mass flow rate
m
           molecular weight
M
           Mach number
M
           number of moles
n
           polytropic exponent
n
P
           pressure
           partial pressure of component i in a mixture
P_{i}
           potential energy
PE
           relative pressure as used in gas tables
           heat transfer per unit mass and total heat transfer
q, Q
           rate of heat transfer
0
```

	Q_H, Q_L $\frac{R}{R}$ S, S S_{gen} S_{gen} t T u, U v, V v_r v v v v v v v	heat transfer with high-temperature body and heat transfer with low-temperature body; sign determined from context gas constant universal gas constant specific entropy and total entropy entropy generation rate of entropy generation time temperature specific internal energy and total internal energy specific volume and total volume relative specific volume as used in gas tables velocity work per unit mass and total work rate of work, or power reversible work between two states quality gas-phase mole fraction elevation compressibility factor electrical charge
SCRIPT LETTERS	E F T	electrical potential surface tension tension
GREEK LETTERS	$egin{array}{l} lpha \ lpha_p \ eta' \ eta_S \ eta_T \ \eta \ \mu \ u \ ho \ \Phi \ \phi \ , \Phi \ \psi \ \omega \ \omega \end{array}$	residual volume volume expansivity coefficient of performance for a refrigerator coefficient of performance for a heat pump adiabatic compressibility isothermal compressibility efficiency chemical potential stoichiometric coefficient density equivalence ratio relative humidity exergy or availability for a control mass flow availability humidity ratio or specific humidity a centric factor
SUBSCRIPTS	c c.v. e f	property at the critical point control volume state of a substance leaving a control volume formation

f	property of saturated liquid
fg	difference in property for saturated vapor and saturated liquid
g	property of saturated vapor
i	state of a substance entering a control volume
i	property of saturated solid
if	difference in property for saturated liquid and saturated solid
ig	difference in property for saturated vapor and saturated solid
r	reduced property
S	isentropic process
0	property of the surroundings
0	stagnation property
	bar over symbol denotes property on a molal basis (over V, H, S, U, A, G, the
	bar denotes partial molal property)
0	property at standard-state condition
*	ideal gas
*	property at the throat of a nozzle
rev	reversible

SUPERSCRIPTS

FUNDAMENTALS OF THERMODYNAMICS

SIXTH EDITION

CONTENTS

1	Som	IE INTRODUCTORY COMMENTS	1
	1.1	The Simple Steam Power Plant, 1	
	1.2	Fuel Cells, 2	
	1.3	The Vapor-Compression Refrigeration Cycle, 5	
	1.4	The Thermoelectric Refrigerator, 7	
	1.5	The Air Separation Plant, 8	
	1.6	The Gas Turbine, 9	
	1.7	The Chemical Rocket Engine, 11	
	1.8	Other Applications and Environmental Issues, 12	
2	SOM	IE CONCEPTS AND DEFINITIONS	14
	2.1	A Thermodynamic System and the Control Volume, 14	
	2.2	Macroscopic Versus Microscopic Point of View, 15	
	2.3	Properties and State of a Substance, 16	
	2.4	Processes and Cycles, 17	
	2.5	Units for Mass, Length, Time, and Force, 18	
	2.6	Energy, 21	
	2.7	Specific Volume and Density, 23	
	2.8	Pressure, 25	
	2.9	Equality of Temperature, 31	
	2.10	The Zeroth Law of Thermodynamics, 31	
	2.11	Temperature Scales, 32	
	Probl	ems, 34	
3	PRO	PERTIES OF A PURE SUBSTANCE	43
	3.1	The Pure Substance, 44	
	3.2	Vapor-Liquid-Solid-Phase Equilibrium in a Pure Substance, 44	
	3.3	Independent Properties of a Pure Substance, 51	
	3.4	Tables of Thermodynamic Properties, 51	
	3.5	Thermodynamic Surfaces, 59	
	3.6	The P-V-T Behavior of Low- and Moderate-Density Gases, 61	
		Computerized Tables, 69	
	Probl	ems, 72	
4	Wol	RK AND HEAT	84
	4.1	Definition of Work, 84	
	4.2	Units for Work, 86	
	4.3	Work Done at the Moving Boundary of a Simple Compressible Syste	m, 87
	4.4	Other Systems that Involve Work, 96	
	4.5	Concluding Remarks Regarding Work, 98	

4.6

Definition of Heat, 100

	4.7	Heat Transfer Modes, 101	
	4.8	Comparison of Heat and Work, 103	
	Prob	lems, 105	
5	THE	E FIRST LAW OF THERMODYNAMICS	116
	5.1	The First Law of Thermodynamics for a Control Mass Undergoing a Cycle, 116	
	5.2	The First Law of Thermodynamics for a Change in State of a Control Ma	ss, 117
	5.3	Internal Energy—A Thermodynamic Property, 124	
	5.4 5.5	Problem Analysis and Solution Technique, 126	
	5.6	The Thermodynamic Property Enthalpy, 130 The Constant-Volume and Constant-Pressure Specific Heats, 133	
	5.7	The Internal Energy, Enthalpy, and Specific Heat of Ideal Gases, 135	
	5.8	The First Law as a Rate Equation, 141	
	5.9	Conservation of Mass, 143	
	Prob	lems, 145	
6	FIRS	ST LAW ANALYSIS FOR A CONTROL VOLUME	162
	6.1	Conservation of Mass and the Control Volume, 162	
	6.2	The First Law of Thermodynamics for a Control Volume, 165	
	6.3	The Steady-State Process, 167	
	6.4	Examples of Steady-State Processes, 169	
	6.5 Prob1	The Transient Process, 183 ems, 195	
	F1001	ems, 193	
7	THE	SECOND LAW OF THERMODYNAMICS	214
	7.1	Heat Engines and Refrigerators, 214	
	7.2	The Second Law of Thermodynamics, 220	
	7.3	The Reversible Process, 223	
	7.4 7.5	Factors that Render Processes Irreversible, 224 The Carnot Cycle, 227	
	7.6	Two Propositions Regarding the Efficiency of a Carnot Cycle, 229	
	7.7	The Thermodynamic Temperature Scale, 230	
	7.8	The Ideal-Gas Temperature Scale, 233	
	7.9	Ideal versus Real Machines, 236	
	Probl	ems, 240	
8	ENT	ROPY	251
	8.1	The Inequality of Clausius, 251	
	8.2	Entropy—A Property of a System, 255	
	8.3	The Entropy of a Pure Substance, 257	
	8.4 8.5	Entropy Change in Reversible Processes, 259 The Thermodynamic Property Relation, 263	
	0)	THE THERMOGYNAMIC Property Kelation 763	

	8.6 8.7 8.8 8.9 8.10 8.11 8.12 Proble	Entropy Change of a Control Mass During an Irreversible Process, 26-Entropy Generation, 266 Principle of the Increase of Entropy, 268 Entropy Change of a Solid or Liquid, 272 Entropy Change of an Ideal Gas, 273 The Reversible Polytropic Process for an Ideal Gas, 278 Entropy as a Rate Equation, 282 ems, 285	4
9	9.1 9.2 9.3 9.4 9.5 9.6	The Second Law of Thermodynamics for a Control Volume, 302 The Steady-State Process and the Transient Process, 304 The Reversible Steady-State Process, 313 Principle of the Increase of Entropy, 316 Efficiency, 317 Some General Comments Regarding Entropy, 323 ems, 325	302
10	10.1 10.2 10.3	VERSIBILITY AND AVAILABILITY Available Energy, Reversible Work, and Irreversibility, 343 Availability and Second-Law Efficiency, 355 Exergy Balance Equation, 363 ems, 370	343
11	11.1 11.2 11.3 11.4 11.5 11.6 11.7 11.8 11.9 11.10 11.11 11.12 11.13 11.14 11.15 11.16 11.17	Introduction to Power Systems, 382 The Rankine Cycle, 384 Effect of Pressure and Temperature on the Rankine Cycle, 388 The Reheat Cycle, 393 The Regernative Cycle, 396 Deviation of Actual Cycles from Ideal Cycles, 403 Cogeneration, 409 Air-Standard Power Cycles, 410 The Brayton Cycle, 411 The Simple Gas-Turbine Cycle with a Regenerator, 418 Gas-Turbine Power Cycle Configurations, 421 The Air-Standard Cycle for Jet Propulsion, 424 Reciprocating Engine Power Cycles, 426 The Otto Cycle, 427 The Diesel Cycle, 431 The Stirling Cycle, 433 Introduction to Refrigeration Systems, 434 The Vapor-Compression Refrigeration Cycle, 435 Working Fluids for Vapor-Compression Refrigeration Systems, 438	382

	11.21 11.22	Deviation of the Actual Vapor-Compression Refrigeration Cycle from the Ideal Cycle, 439 The Ammonia Absorption Refrigeration Cycle, 441 The Air-Standard Refrigeration Cycle, 442 Combined-Cycle Power and Refrigeration Systems, 446	
		ems, 450	
12	GAS	MIXTURES	473
	12.1 12.2 12.3 12.4 12.5 12.6 Proble	General Considerations and Mixtures of Ideal Gases, 473 A Simplified Model of a Mixture Involving Gases and a Vapor, 480 The First Law Applied to Gas-Vapor Mixtures, 485 The Adiabatic Saturation Process, 488 Wet-Bulb and Dry-Bulb Temperatures, 490 The Psychrometric Chart, 491 ems, 494	
13	THE	RMODYNAMIC RELATIONS	511
	13.1	The Clapeyron Equation, 511	
	13.2	Mathematical Relations for a Homogeneous Phase, 515	
	13.3	The Maxwell Relations, 516	
	13.4	Thermodynamic Relations Involving Enthalpy, Internal Energy, and Entropy, 519	
	13.5	Volume Expansivity and Isothermal and Adiabatic Compressibility, 52	24
	13.6	Real Gas Behavior and Equations of State, 527	
	13.7	The Generalized Chart for Changes of Enthalpy at Constant	
		Temperature, 532	
	13.8	The Generalized Chart for Changes of Entropy at Constant	
		Temperature, 535	
	13.9	Developing Tables of Thermodynamic Properties from Experimental Data, 538	
	13.10	The Property Relation for Mixtures, 540	
	13.11	Pseudopure Substance Models for Real-Gas Mixtures, 543	
	Proble	ems, 550	
14	CHE	MICAL REACTIONS	561
	14.1	Fuels, 561	
	14.2	The Combustion Process, 564	
	14.3	Enthalpy of Formation, 572	
	14.4	First-Law Analysis of Reacting Systems, 574	
	14.5	Enthalpy and Internal Energy of Combustion; Heat of Reaction, 581	
	14.6	Adiabatic Flame Temperature, 585	
	14.7	The Third Law of Thermodynamics and Absolute Entropy, 587	
	14.8	Second-Law Analysis of Reacting Systems, 589	
	14.9	Fuel Cells, 596	
		Evaluation of Actual Combustion Processes, 599	
	Proble	ems 604	