

Basic Engineering Thermodynamics

SECOND EDITION

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McGRAW-HILL
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This book was set in Modern by Maryland Composition Incorporated.
The editors were B. J. Clark and J. W. Maisel;
the cover was designed by Ben Kann;
the production supervisor was Leroy A. Young.
New drawings were done by Eric G. Hieber Associates Inc.
Kingsport Press, Inc., was printer and binder.

Library of Congress Cataloging in Publication Data

Zemansky, Mark Waldo, date
Basic engineering thermodynamics.

Includes bibliographical references.

I. Thermodynamics. I. Abbott, Michael M., joint author. II. Van Ness, Hendrick C., joint author. III. Title.

TJ265.Z54 1975 621.4'021 74-13559
ISBN 0-07-072815-1

**BASIC
ENGINEERING
THERMODYNAMICS**

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234567890KPKP798765

PREFACE

It has been our purpose to prepare a textbook for an initial course in thermodynamics for engineers of any discipline. Such a course must stress the fundamental principles of thermodynamics and, at the same time, be of sufficient breadth to prepare students for a variety of subsequent courses in which the principles are applied to different kinds of systems. Thus, while paying ample attention to simple fluid systems, we have also included careful treatments of solid systems under stress, surfaces, cells, and electric and magnetic systems.

We have been guided in our presentation of the fundamental principles of thermodynamics by Zemansky's "Heat and Thermodynamics," a widely used introductory text of some forty years standing for students of science. The present work is in some measure an engineering adaptation of that work. Since this work is designed for use in engineering curricula, emphasis is placed on a variety of applications of technological significance.

The main body of the text is devoted to the principles and applications of classical thermodynamics, an area of study which in no way depends on the atomistic nature of matter. The final chapter presents an elementary discussion of statistical thermodynamics, which owes its existence

to atomic and quantum theory. Its purpose is to provide an introduction to a branch of knowledge in which may be found a deeper insight into the nature of the laws of thermodynamics.

Although many individuals have contributed in one way or another, by question or comment, to the quality of this second edition of "Basic Engineering Thermodynamics," no one has approached the helpfulness of Howard E. Cyphers, Associate Professor of Mechanical Engineering at Rensselaer Polytechnic Institute, who studied the manuscript with an eagle eye and directed our attention to numerous errors and infelicities.

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LIST OF SYMBOLS

Capital Italics

| | |
|---------------|--|
| A | Helmholtz function; area |
| B, B' | Second virial coefficient |
| \mathcal{B} | Dimensionless second virial coefficient |
| B^0, B^1 | Functions of T_r in the Pitzer correlation for B |
| C, C' | Heat capacity; third virial coefficient |
| D, D' | Fourth virial coefficient |
| E | Young's modulus; energy |
| E' | Unavailable energy |
| E_K | Kinetic energy |
| E_P | Gravitational potential energy |
| F | Force; fluid friction; degrees of freedom |
| G | Gibbs function |
| H | Enthalpy |
| H' | Enthalpy in ideal-gas state |
| \hat{H} | Generalized enthalpy |
| I | Current |

| | |
|--------------------|--|
| K | Equilibrium constant |
| L | Length |
| M | General designation of thermodynamic function; molecular weight |
| M' | General designation of thermodynamic function in ideal-gas state |
| M^t | General designation of total thermodynamic property of a system |
| N | Number of particles |
| N_0 | Avogadro's number |
| P | Pressure; probability |
| P_c | Critical pressure |
| P_r | Reduced pressure |
| Q | Heat |
| R | Universal gas constant; electric resistance |
| S | Entropy |
| S' | Entropy in ideal-gas state |
| S_{total} | Total entropy of a system and its surroundings |
| T | Absolute temperature |
| T_c | Critical temperature |
| T_r | Reduced temperature |
| U | Internal energy |
| V | Volume |
| \bar{V}_c | Critical volume |
| V_r | Reduced volume |
| W | Work |
| W_s | Shaft work |
| X | Generalized displacement coordinate |
| Y | Generalized force coordinate |
| Z | Compressibility factor |
| Z_c | Critical compressibility factor |

Lowercase Italics

| | |
|-----|---|
| a | Acceleration |
| c | Speed of sound |
| d | Sign for an exact differential |
| e | Electromotive force |
| f | As subscript, identifies liquid water |
| g | Acceleration of gravity; degeneracy; as subscript, identifies water vapor |
| h | Planck's constant; height |
| i | As subscript, identifies a chemical species or an energy level |
| j | Moles of electrons transferred in a cell per mole of reaction advancement |

| | |
|-------|---|
| k | Boltzmann's constant; proportionality constant |
| l | Length; as superscript, identifies a liquid phase |
| m | Mass; number of chemical species |
| n | Number of moles |
| n_q | Number of ensembles in quantum state q |
| p_i | Partial pressure |
| q | Electric charge; as subscript, identifies a quantum state |
| r | Radius; compression ratio |
| s | As superscript, identifies a solid phase |
| t | Celsius or Fahrenheit temperature; as superscript, identifies a total system property |
| u | Velocity |
| v | Potential difference; as superscript, identifies a vapor phase |
| x | Distance; quality |
| x_i | Mole fraction of species i in liquid phase |
| y_i | Mole fraction of species i in vapor phase |
| z | Elevation above a datum level |

Script Capitals

| | |
|---------------|----------------------------------|
| \mathcal{B} | Magnetic induction |
| \mathcal{C} | Curie constant |
| \mathcal{D} | Electric displacement |
| \mathcal{E} | Electric field strength |
| \mathcal{F} | Faraday's constant |
| \mathcal{H} | Magnetic field strength |
| \mathcal{M} | Total Magnetization |
| \mathcal{N} | Number of systems in an ensemble |
| \mathcal{P} | Total Polarization |
| \mathcal{S} | Ensemble entropy |
| \mathcal{U} | Ensemble internal energy |
| \mathcal{Z} | System partition function |

Special Symbols

| | |
|------------------|--|
| \ln | Natural logarithm (base e) |
| \log | Common logarithm (base 10) |
| M | Mach number |
| $\Delta H'$ | Residual enthalpy $\equiv H' - H$ |
| $\Delta M'$ | Residual property in general $\equiv M' - M$ |
| $\Delta S'$ | Residual entropy $\equiv S' - S$ |
| ΔG° | Standard Gibbs function change of reaction $\equiv \sum \nu_i G_i^\circ$ |

| | |
|---------------------------|--|
| ΔH° | Standard heat of reaction $\equiv \sum \nu_i H_i^\circ$ |
| $\Delta H^{\alpha\beta}$ | Latent heat of phase change $\equiv H^\beta - H^\alpha$, also $\Delta H_{\alpha\beta}$ |
| $\Delta S^{\alpha\beta}$ | Entropy change of phase change $\equiv S^\beta - S^\alpha$, also $\Delta S_{\alpha\beta}$ |
| $\Delta V^{\alpha\beta}$ | Volume change of phase change $\equiv V^\beta - V^\alpha$, also $\Delta V_{\alpha\beta}$ |
| ΔS_{total} | Total entropy change of a system and its surroundings |
| T^* | Magnetic temperature |
| | Designates an absolute value |
| { } | Designates a {set} of values |
| . | Designates a time derivative or rate |
| ' | Designates a value for the ideal-gas state |
| ° | Designates the standard state |

Greek Letters

| | |
|--------------|--|
| α | Linear expansivity; as superscript, identifies a phase |
| β | Volume expansivity; as superscript, identifies a phase |
| γ | Ratio of heat capacities, C_P/C_V ; surface tension |
| δ | Sign for an inexact differential; linear compressibility |
| Δ | Finite-difference sign |
| ϵ | Strain; reaction coordinate |
| ϵ_0 | Permittivity of vacuum |
| η | Efficiency |
| θ | Empiric temperature |
| κ | Isothermal compressibility |
| κ_S | Adiabatic compressibility |
| μ | Joule-Kelvin coefficient; chemical potential |
| μ_0 | Permeability of vacuum |
| ν_i' | Stoichiometric coefficient |
| ν_i | Stoichiometric number |
| ν | $\equiv \sum \nu_i$ |
| Π | Continuous-product sign |
| π | Number of phases |
| ρ | Density |
| Σ | Summation sign |
| σ | Stress; deviation |
| τ | Time |
| χ_e | Electric susceptibility |
| χ_m | Magnetic susceptibility |
| ω | Acentric factor; number of ensemble arrangements; coefficient of performance |

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Mollier Diagram for Steam (back endpapers)

1-1 Macroscopic Point of View

The application of scientific principles to the solution of any real problem must necessarily start with a separation of a restricted region of space or a finite portion of matter from its surroundings. The portion which is set aside (in the imagination) and on which attention is focused is called the *system*, and everything outside the system which has a direct bearing on its behavior is known as the *surroundings*. When a system has been chosen, the next step is to describe it in terms of quantities related to the behavior of the system or its interactions with the surroundings, or both. There are in general two points of view that may be adopted, the *macroscopic* and the *microscopic*.

Let us take as a system the contents of a cylinder of an automobile engine. A chemical analysis would show a mixture of hydrocarbons and air before explosion, and after the mixture had been ignited there would be combustion products describable in terms of certain chemical compounds. A statement of the relative amounts of these substances is a description of the *composition* of the system. At any moment, the system whose composition has just been described occupies a certain *volume*, depending on the position of the piston. The volume can be easily measured and, in the laboratory, is recorded automatically by means of an appliance coupled to the piston. Another quantity that is indispensable in the description of our system is the *pressure* of the gases in the cylinder. After explosion this pressure is large; after exhaust it is small. In the laboratory, a pressure gauge may be used to measure the changes of pressure and to make an automatic record as the engine operates. Finally, there is one more quantity without which we should have no adequate idea of the operation of the engine: the *tem-*

perature. As we shall see, in many instances, it can be measured just as simply as the other quantities.

We have described the materials in a cylinder of an automobile engine by specifying four quantities: composition, volume, pressure, and temperature. These quantities refer to the gross characteristics, or large-scale properties, of the system and provide a *macroscopic description*. They are therefore called *macroscopic coordinates*. The quantities that must be specified to provide a macroscopic description of other systems are, of course, different; but macroscopic coordinates in general have the following characteristics in common:

- 1 They involve no special assumptions concerning the structure of matter.
- 2 They are few in number.
- 3 They are suggested more or less directly by our sense perceptions.
- 4 They can in general be directly measured.

In short, a macroscopic description of a system involves the specification of a *few fundamental measurable properties* of a system. Although the macroscopic point of view is the one adopted in thermodynamics, it should be understood that the microscopic point of view is of great value and that it may lead to a deeper insight into the principles of thermodynamics. This point of view is taken in the branch of science called *statistical mechanics*, a subject considered briefly in the final chapter. We indicate here merely the distinction between the two points of view by giving a simple microscopic description of a gas in a containing vessel.

1-2 Microscopic Point of View

We assume that the gas consists of an enormous number N of particles called molecules, all having the same mass and each moving with a velocity independent of the others. The position of any molecule is specified by the three cartesian coordinates x , y , and z , and the velocity by the three components v_x , v_y , and v_z . Therefore, to describe the position and velocity of a molecule, we need six numbers. A microscopic description of the state of the gas consists of the specification of these six numbers for each of the N molecules.

We need not pursue the matter further to understand that a microscopic description involves the following characteristics:

- 1 Assumptions are made concerning the structure of matter; e.g., the existence of molecules is assumed.

- 2 Many quantities must be specified.
- 3 The quantities specified are not suggested by our sense perceptions.
- 4 These quantities cannot be measured.

1-3 Macroscopic versus Microscopic

Although it might seem that the two points of view are hopelessly different and incompatible, there is, nevertheless, a relation between them, and when both points of view are applied to the same system, they must lead to the same conclusions. The relation between the two points of view lies in the fact that the few directly measurable properties whose specification constitutes the macroscopic description are really averages over a period of time of a large number of microscopic characteristics. For example, the macroscopic quantity pressure is the average rate of change of momentum due to all the molecular collisions made on a unit of area. Pressure, however, is a property that is perceived by our senses. We feel the effects of pressure. Pressure was experienced, measured, and used long before scientists and engineers had reason to believe in the existence of molecular impacts. If molecular theory is changed or even discarded at some time in the future, the concept and meaning of pressure will likely remain. Herein lies an important distinction between the macroscopic and microscopic points of view. The few measurable macroscopic properties are as sure as our senses. They will remain unchanged as long as our senses remain the same. The microscopic point of view, however, goes much further than our senses. It postulates the existence of molecules, their motion, collisions, etc. It is constantly being changed, and we can never be sure that the assumptions are justified until we have compared some deduction made on the basis of these assumptions with a similar deduction based on observed macroscopic behavior.

1-4 Scope of Thermodynamics

It has been emphasized that a description of the gross characteristics of a system by means of a few of its measurable properties, suggested more or less directly by our sense perceptions, constitutes a macroscopic description. Such descriptions are the starting point of all investigations in all branches of science and engineering. For example, in dealing with the mechanics of a rigid body, we adopt the macroscopic point of view in that only the external aspects of the rigid body are considered. The position of its center of mass is specified with reference to coordinate axes at a particular time.