HEAT AND THERMODYNAMICS

An Intermediate Textbook

Sixth Edition

Mark W. Zemansky, Ph.D.

Richard H. Dittman, Ph.D.

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PREFACE

Early textbooks on "heat" devoted many chapters to discussions of thermometry, calorimetry, and heat engines, included many experimental details, and ended with one or two chapters in which an attempt was made to construct a deductive theory, known as "thermodynamics." In these two divisions only the large-scale characteristics of matter were considered, so that both divisions were strictly "macroscopic." In later years, when molecular theory was better understood, the subject matter of statistical mechanics and of kinetic theory was included in the field. Since these two subjects are microscopic in point of view, a more general term was needed to include the four divisions: heat, thermodynamics, statistical mechanics, and kinetic theory. The term most widely used today for this purpose is "thermal physics." Of course, there is no hard and fast rule concerning the relative weights of each of the divisions of thermal physics. Some authors regard statistical mechanics and kinetic theory of primary importance, with heat and thermodynamics a somewhat necessary evil. Others, feeling guilty about their worship of statistical mechanics, hide behind the misnomer "statistical thermodynamics," which seems to refer to a subject that is both microscopic and macroscopic at the same time.

In the present volume, thermodynamics constitutes about 50 percent, heat about 37 percent, statistical mechanics about 10 percent, and kinetic theory about 3 percent. The main reason for this distribution is the deep conviction on the part of the authors that the fundamental foundation of the subject is thermodynamics, which is well within the abilities of undergraduate students. At the sophomore or junior level students have sufficient physical and mathematical sophistication to prepare them for thermodynamic arguments and proofs, whereas they are not quite ready for the subtleties of ergodic theory or of Gibbsian ensembles. Only the simplest treatment of weakly interacting particles is given and applied to an ideal gas, an electron gas, blackbody radiation, a vibrating lattice, and a paramagnetic-ion subsystem in a crystal. This sixth edition contains about the same amount of engineering, chemistry, and experimental detail as its predecessor, but the subjects of superfluidity and superconductivity have been deleted, on the ground that their treatment is no longer exclusively thermodynamic.

The two main features of this sixth edition are: (1) the almost complete use of SI units in all parts of the subject, with the exception of a few topics in chemical thermodynamics; and (2) the subdivision of the book into two almost-equal sections, the first part being devoted to fundamental concepts, designed to be the core of an introductory course in thermodynamics, and the second part, starting with a chapter on elementary statistical mechanics, designed to enable the teacher to choose those applications which require the use of thermodynamics *and* statistical mechanics, such as specific heats of solids, cryogenics, nuclear paramagnetism, and negative temperatures, to name a few. Part 2 also contains such topics as chemical equilibrium, ideal-gas reactions, phase theory, the third law, fuel cells, thermocouples, blackbody radiation, and negative Kelvin temperatures.

The authors would like to express their appreciation of the expertise, understanding, and kindness displayed by the McGraw-Hill staff in the preparation of this book—particularly Marian Provenzano and Scott Amerman. The end-papers contain eighteen pictures of world-famous pioneers in thermodynamics and statistical mechanics. The authors are very grateful to Professor Peter T. Landsberg of Southampton University and to Joan Warnow of the American Institute of Physics for supplying us with these pictures.

Mark W. Zemansky
Richard H. Dittman

NOTATION

CAPITAL ITALIC

A	Area; paramagnetic heat-capacity constant
B	Second virial coefficient; Brillouin function
C	Heat capacity; critical point
D	Debye function; electric displacement
E	Electric intensity; energy
F	Helmholtz function
G	Gibbs function
H	Enthalpy
I	Current; nuclear quantum number
J	Electronic quantum number
K	Thermal conductivity; equilibrium constant
L	Length; latent heat; coupling coefficients
M	Magnetization; mass
N	Number of molecules
P	Pressure
Q	Heat

LOWERCASE ITALIC

a	A dimension; $g\mu_B \mu_0 \mathcal{H}/kT$
b	A dimension; a constant
c	Molar heat capacity; speed of light
d	Differential sign
e	Naperian logarithm base; electronic charge
f	Molar Helmholtz function; variance
g	Molar Gibbs function; Landé *g* factor; degree of degeneracy
h	Molar enthalpy; Planck's constant
i	Vapor-pressure constant
j	Valence
k	Boltzmann's constant
l	Latent heat per kilogram or per mole
m	Mass of a molecule or electron
n	Number of moles; quantum number
p	Partial pressure; momentum
q	Heat per mole

R	Universal gas constant; electric resistance; radius	r	Radius; number of individual reactions
S	Entropy	s	Molar entropy
T	Kelvin temperature	t	Celsius temperature; empirical temperature
U	Internal energy	u	Molar energy; radiant-energy density
V	Volume	v	Molar volume
W	Work	w	Speed of a wave or a molecule
X	Generalized displacement	x	Space coordinate; mole fraction
Y	Generalized force; Young's modulus	y	Space coordinate; fraction
Z	Electric charge; partition function; compressibility factor	z	Space coordinate

SCRIPT CAPITALS

$\mathscr{B}$	Magnetic induction
$\mathscr{E}$	Electromotive force
$\mathscr{F}$	Tension; force
$\mathscr{H}$	Magnetic intensity
$\mathscr{M}$	Molar mass or molecular weight
$\mathscr{R}$	Radiant exitance
$\mathscr{S}$	Surface tension

ROMAN SYMBOLS FOR UNITS

m	meter
kg	kilogram
s	second
atm	atmosphere
A	ampere
A/m	ampere · turn per meter
C	coulomb
Hz	hertz (cps)
J	joule
N	newton
Pa	Pascal
T	tesla
V	volt
W	watt

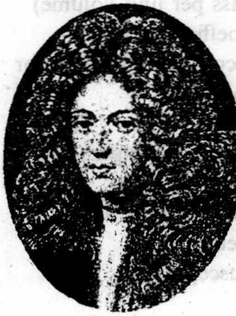
SPECIAL SYMBOLS

N_A	Avogadro's number
$đ$	Inexact differential
N_F	Faraday's constant
T^*	Magnetic temperature
C_C'	Curie constant

GREEK LETTERS

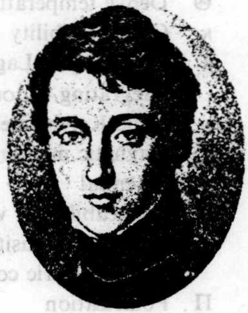
α	Linear expansivity; critical-point exponent
β	Volume expansivity; $1/kT$; critical-point exponent
γ	Ratio of heat capacities; electronic term in heat capacity; critical-point exponent
Ω	Thermodynamic probability; solid angle
δ	Energy of a magnetic ion; critical-point exponent
Δ	Finite difference
ϵ	Degree of reaction; molecular energy; reduced temperature difference; Seebeck coefficient
η	Efficiency

θ	Ideal-gas temperature; angle
Θ	Debye temperature
κ	Compressibility
λ	Wavelength; Lagrange multiplier; integrating factor
μ	Joule-Kelvin coefficient; molecular magnetic moment; chemical potential
μ_0	permeability of vacuum
ν	Molecular density; frequency; stoichiometric coefficient
Π	Polarization
π	Peltier coefficient
ρ	Density (mass per unit volume)
σ	Thomson coefficient; Stefan-Boltzmann constant; function for isentropic surface
τ	Time; period
ϕ	Angle; function of temperature
φ	Number of phases
ω	Coefficient of performance; angular speed
χ	Magnetic susceptibility



Robert Boyle
1627-1691

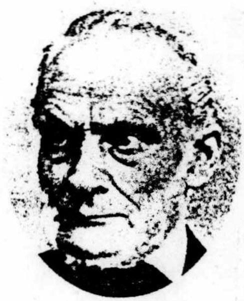
Benjamin Thompson Count Rumford 1753-1814



Nicolas Léonard Sadi Carnot 1796-1832

James P. Joule
1818-1889

Hermann L. F. von Helmholtz
1821-1894



Rudolf Clausius
1822-1888

Gustav Robert Kirchhoff 1824-1887

William Thomson Lord Kelvin 1824-1907

Clerk Maxwell
1831-1879

Josiah Willard Gibbs 1839-1903

Ludwig Boltzmann
1844-1906

Heikè Kamerlingh Onnes
1853-1926

Max Planck
1858-1947

Walther Nernst
1864-1941

Constantin Carathéodory
1873-1950

Albert Einstein
1879-1955

Peter Debye
1884-1966

Francis E. Simon
1893-1956

CONTENTS

PART ONE

FUNDAMENTAL CONCEPTS