时代教育 • 国外高校优秀教材精选

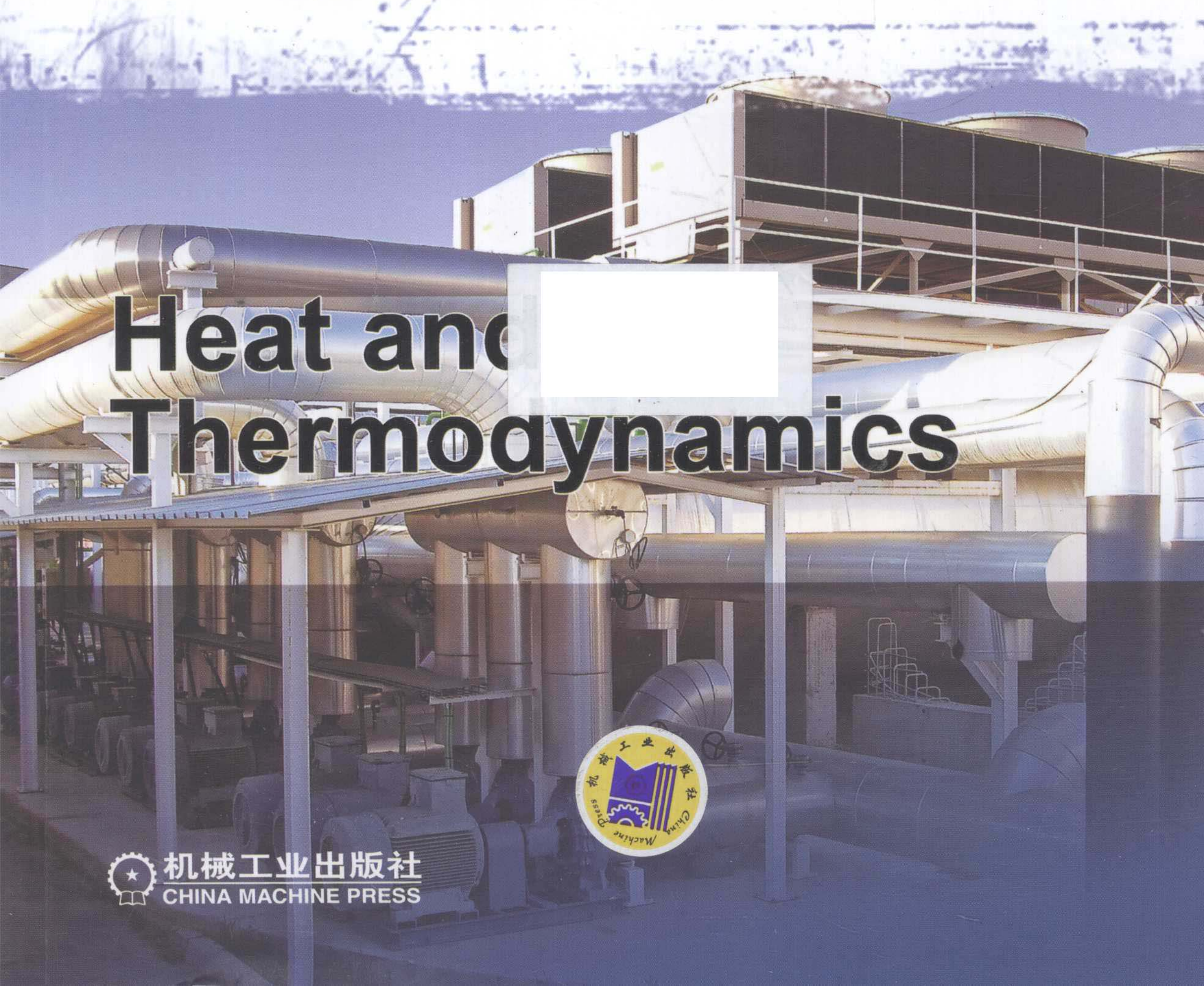
McGraw Hill Education

热与热力学

(英文影印版 • 原书第8版)

[美] M. W. 齐曼思基 (Mark W. Zemansky)
R. H. 迪特曼 (Richard H. Dittman) 著

Heat and Thermodynamics



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传统上，这本教科书一直致力于介绍热力学和统计物理学所选主题。内容包括温度和热力学第零定律、简单热力学系统、功、热能和热力学第一定律、理想气体、热力学第二定律、卡诺循环与热力学温标、熵、理想物质与真实物质、热力学关系、气体的动力学理论、开放系统、统计力学、固体的热学性质、临界现象、化学平衡、理想气体反应、异构系统等内容。

本书可作为物理学、应用物理学，以及工程热物理相关专业的教材或教学参考书。

Mark W. Zemansky
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关于作者

M. W. 齐曼思基（MARK W. ZEMANSKY）

1900 年出生于纽约，1921 年毕业于纽约城市大学，并在 1927 年获哥伦比亚大学博士学位。除了 1928 年至 1930 年在普林斯顿大学以及 1930 年和 1931 年在柏林凯撒威廉研究所深造外，从 1925 年直至 1967 年退休，一直在纽约城市大学任职。1937 年完成《热与热力学》（*Heat and Thermodynamics*）第 1 版。1947 年，与 F. W. 西尔斯（Francis W. Sears）合作出版《物理学》（*College Physics*）第 1 版，两年后出版《大学物理》（*University Physics*）。1941 年至 1947 年间任《美国物理学杂志》（*American Journal of Physics*）副主编，1951 年任美国物理教师协会会长，并在 1967 年至 1970 年担任执行秘书。逝于 1981 年。

R. H. 迪特曼（RICHARD H. DITTMAN）

1937 年出生于加利福尼亚州萨克拉门托，1959 年毕业于圣塔克拉拉大学，并于 1965 年获圣母大学博士学位。随后的一年里在柏林弗里茨哈伯研究所做研究工作，然后进入密尔沃基的威斯康辛大学任职，直到现在。与 G. M. 施密克（Glenn M. Schmieg）合作，于 1979 年完成了《你身边的物理》（*Physics in Everyday Life*）一书。分别于 1971 年和 1989 年两次荣获杰出教师教学奖。同时，还担任威斯康辛大学物理系主任和文理学院副院长等职。

A. K. 查托帕迪亚雅（AMIT K. CHATTOPADHYAY）

1973 年出生于印度西孟加拉邦钦苏拉，1995 年在加尔各答大学塞兰布尔学院获学士学位。紧接着，1997 年又在该校获物理学硕士学位。2001 年，在加尔各答的印度科学培养协会获得博士学位，主攻理论物理。做博士后期间，曾先后在德国德累斯顿的普朗克研究所从事复杂系统物理研究，在柏林哈恩-迈特纳研究所做洪堡学者，以及在英国华威大学和意大利帕多瓦大学进行合作研究。另外，作者还是首位荣获欧洲最高科研奖励——玛丽·居里奖学金的印度人。在做博士后的最后阶段，作者在英国爱丁堡大学获得一个长期职位。2007 年，作者决定回到家乡，并在德里大学得到一个副教授职位。同时他还是英国阿斯顿大学的讲师，主要研究方向是复杂系统。

PREFACE TO THE EIGHTH EDITION

Overview of the Subject

Traditionally, this has been a textbook devoted to thermodynamics and chosen topics on statistical physics where the latter element comes more into focus with evolving editions. In the present volume, I have endeavoured to maintain this *classical* flavour while at the same time ensured that novel advancements in these subjects are also brought to the forefront. The emphasis still is on thermodynamics, a subject that construes the foundation of modern *many-body physics*; while the later statistical physics sections, along with giving a microscopic foundation to thermodynamics, focus both on solved and open problems in quantum *many-body physics*.

Here the focus, as is evident from the examples chosen, is on solid-state physics. While designing a plan for this new edition, I dallied with the complementary option of using more sophisticated tools borrowed from *field theory* in discussing the macroscopic thermodynamic observations, as has been the *suo moto* in many recent such textbooks. But I chose to remain 'old fashioned' in an attempt to not confuse the starting undergraduate minors. For the more advanced students, though, carefully chosen examples, based on the principles of field theory, have now been inducted to give a hands-on approach to these advanced ideas.

This has been a time-tested classic in thermal physics and a major incentive of this adaptation volume has been to focus on the needs of Indian students and universities with changing times. The challenge was nontrivial. On the one hand, I had to make sure that the classical finesse is retained while simultaneously making sure that at least some extract of related modern researches do percolate to the level of an interested undergraduate student.

Roadmap for Target Courses

The present edition has been structured according to UGC guidelines and covers the Indian undergraduate curriculum in its entirety. The more advanced sections involving kinetic theory (Chapter 11) and statistical mechanics (Chapter 13 onwards), are generally intended for the advanced undergraduate or the first year post-graduate syllabus. Project works, which form an integral part of university studies these days, could well benefit from the chapter on the kinetic theory of gases and Appendices A to D. Some of the unsolved problems are even without known exact results and are meant to act as fodder for thought for our budding physicists. They would also do themselves a favor by (at least occasionally) having a go at the additional reference materials suggested.

The present edition, admittedly, is problem heavy. That is the way the subject has evolved and the present author believes, that is how it should be. If that is accepted as a (Tripos like) hypothesis, the students then have a right to expect such problem oriented preparation from the text book they buy and this is what this book intends to cater.

Another addition that I pondered and unfortunately, had to decide against, was the incorporation of problems that would have needed the use of computer programming skills. The problems here are manifold: there is no known UGC guideline as to the programming language, so each university has its own choice. For the same reason, most of the competitive examinations are not too keen on having computer-oriented problems, albeit it would be immensely helpful and riveting to see numbers generated in the computer that agree with the studied theory. This is a plan for the future and subject to suitable interest could make its way in the next edition.

New to this Edition

This edition has undergone a major revamp in the form of a completely new chapter on the *kinetic theory of gases*, a most important topic largely overlooked in all previous editions. There is a specific reason for which I chose to include this subject. I intend to make this textbook a bridge in between thermal physics and the more challenging world of time-dependent non-equilibrium physics, on which much of the modern-day *complex systems* research is focused. A familiarity with such language could open up a vast realm of diverse worlds ranging from mathematical biology to stochastic financial time-series analysis. I have been careful, though, to retain the grand old structure of this book in providing few examples and leaving a few challenging ones unsolved in the Appendix. The chapter is divided into two sectors: an equilibrium section and a non-equilibrium section.

- The equilibrium part starts with a detailed analysis of the *Maxwell-Boltzmann distribution*, its derivation, later application and the importance of statistics in studying large-scale data. This is followed by kinetic derivations of the different gas laws—*ideal gas law*, *Charles's law*, *Boyle's law* and *Avogadro's law*. Using the derivation of the probability density function for the Maxwell–Boltzmann distribution as an example in hand, a more generalized probabilistic structure is now elicited for the case of hard sphere-type interacting particles. The varying nature of such interactions, popularly referred to as *transport phenomena—conduction*, *convection* and *radiation*—are now derived and discussed in detail.

- In the non-equilibrium section, I have focused on topics of long-standing interest, which apart from their importance to academic researchers, are proving to be equally appealing to workers, and not necessarily academic, in more empirical fields studying 'real life' stochastic problems in biology, economics and ecology. The first of these is the *Brownian motion*, studied for 'dilute' gases, both from the view point of a *diffusion equation*, as well as from a probabilistic concept. The case of 'nondilute' gases leads to the more complicated *Boltzmann transport equation*. Here, again, I followed a minimalist approach of conserving the intellectual resources in getting a 'feel' of the problem rather than deductive solutions. The challenge of such technical approach is highlighted in the unsolved problems, possibly for the more inquisitive reader though.

Here is a sequential list of changes effected in this new edition:

- A new appendix (A) detailing the third law of thermodynamics, together with solved and unsolved problems, has been added.
- A new appendix (B) now discusses the concept and effect of a 'negative temperature' in systems showing population inversion.
- Appendix C explains how ultra-low temperatures are industrially achieved using the principle of magnetic cooling by adiabatic demagnetisation.
- A section on *adiabatic lapse rate* forms the basis for a new Appendix D.
- More in the line of stringing a historical development of the subject of classical critical phenomena, Andrews' experiments on CO_2 gas has been discussed in Appendix E.
- The new chapter on the kinetic theory of gases, together with the new appendices, have now been revamped with new problems, both solved and unsolved (often with hints).
- A set of unsolved problems of a more challenging nature is now inducted as a revision mechanism at the end of the book. These problems are randomly distributed with regards to their chapters of origin and often inspired by similar (in motif) problems at international universities.

Salient Features

- Coverage of all fundamental concepts of thermal physics—Temperature and Laws of Thermodynamics, Thermodynamic Systems, Work, Heat, Carnot Cycle, Thermodynamic Temperature scale, Entropy, Pure substances, Mathematical methods, Open systems, Statistical Mechanics, Properties of solids, Phase transitions, Chemical Equilibrium, Ideal Gas reaction, Heterogeneous systems.
- Several topical additions in appendics—Adiabatic Lapse Rate, Refrigeration Cycles, Efficiency, Continuity of Liquid and Gaseous State, Third Law of Thermodynamics, Zero-point Energy, Negative Temperature, Superconductivity.

- Complete problem-solving support
  - Over 50 *new* solved problems introduced in a graded manner
  - Over 200 unsolved problems
  - Stepwise derivation of key formulae within chapters
- Rich pedagogy and ready reckoner tools
  - All key concepts explained through more than 200 phase diagrams, tables and graphs
  - List of physical constants
  - Thermodynamic definitions and formulae
  - Conceptual lists like Lagrangian Multipliers, Evaluation of Integrals, Reimann Zeta Functions

Chapter Organisation

This book is organised into two parts, covering 18 chapters in totality. ***Part I*** deals with **Fundamental Concepts** and consists of chapters 1 to 12. These chapters cover topics like Temperature and the Zeroth Law of Thermodynamics; Simple Thermodynamic Systems; Heat and the First law of Thermodynamics; Ideal Gas; Second Law of Thermodynamics; Carnot Cycle and the Thermodynamic Temperature Scale; Entropy; Kinetic Theory of Gases; Pure Substances; Mathematical Methods and Open Systems.

Part II presents the **Applications of Fundamental Concepts** and contains chapters 13 to 18. These chapters deal with the concepts of Statistical Mechanics; Thermal Properties of Solids; Critical Phenomena—Higher-Order Phase Transitions; Chemical Equilibrium; Ideal-Gas Reactions and Heterogeneous Systems.

Twelve ***Appendices*** are present at the end of the book which contain additional reading material focusing on Physical Constants; Method of Lagrangian Multipliers; Evaluation of the Integral $\int e^{-ax^2} dx$ between the limits 0 and ∞; Riemann Zeta Functions; Thermodynamic Definitions and Formulas; Questions to Ponder; and Miscellaneous Solved Problems.

Apart from this, a **Bibliography** lists the important reference books which interested students may refer to at their discretion. Finally, **Answers to Selected Problems** are given so that students can check out the solutions of the unsolved problems.

Acknowledgements

The preface would remain abjectly incomplete without my special allusions to Renu Upadhyay and Smruti Snigdha, the Development editor: Sponsoring editor team, who virtually goaded this time-lapsing adapter into submission! If not for them, this work would never have been complete.

Further, I would like to thank the complete Tata McGraw-Hill team Ms. Vibha Mahajan, Ms. Shalini Jha, Ms. Sohini Mukherjee and Ms. Anjali Razdan.

From a personal perspective, I am eternally indebted to my wife, Nabanita, and daughter, Aatreyi, for putting up with my most unconventional work hours and non-negligible whims. A special acknowledgement goes also to the University of Delhi since it was during my tenure there that the idea of this book was conceived.

Apart from this, I would also like to thank Francis P Xavier, Loyola College, Chennai; and P C Vinod Kumar, Sardar Patel University, Vallabh Vidyanagar, Gujarat; for their efforts in reviewing this book.

As a student, I too learnt thermodynamics from this textbook and I hope this new edition would serve identically to a new generation. Needless to mention, any error that the students may come across would be mine and any feedback would be most gratefully dealt with.

Amit K Chattopadhyay

Feedback

Do you have a feature request? A suggestion? We are always open to new ideas and the best ideas come from you. Please send your comments to tmh.sciencemathsfeedback@gmail.com request you to please mention the title and author name in the subject line.

Piracy-related issues may also be reported.

PREFACE TO THE SEVENTH EDITION

Mark W Zemansky wrote the first five editions of *Heat and Thermodynamics* and we collaborated on the sixth edition. In this edition, Zemansky's pedagogical philosophy and style were my guide for making revisions. True to his tradition, the primary emphasis is placed on the thermodynamic (macroscopic) study of temperature, energy, and entropy, while recognizing that equations of state, temperature variations of specific heats, and valuable insight come from the statistical mechanical (microscopic) approach. Methods of measurement are explained throughout the book and actual data are given in graphs and tables. Mathematical theorems beyond elementary partial differentiation are derived and explained at places where they are needed.

The sequence of topics in this edition is identical to the last edition and generally follows all previous editions, but changes were made to keep the book up to date or to assist the student. Listed below are the significant additions or changes:

- Replacement of the symbol θ for ideal-gas temperatures by the symbol T for absolute temperatures in the first chapter, before the two quantities are proven equal using the second law.
- Inclusion of the International Temperature Scale of 1990, which defined the practical temperature scale down to 0.65 K and eliminated the thermocouple as a primary standard thermometer.
- Determination of the universal gas constant R from speed of sound measurements. This became the new standard in 1986 and eliminated the method based on the ideal-gas law.
- Expression of the thermal efficiences of internal-combustion engines in terms of temperature rather than compression and expansion ratios, thus providing a better preparation for the Carnot engine.
- Replacement of the axiomatic presentation of the second law of thermodynamics, according to Carathéodory, with the method of Carnot, Clausius, Kelvin, and Planck using cycles in a reversible heat engine.
- Extension of the phase diagram for H_2O to include two very-high-pressure polymorphs of ice.

- Use of Legendre transformations to organize the thermodynamic potentials for closed systems—Internal Energy, Enthalpy, Helmholtz Function, and Gibbs Function; and
- Introduction of four thermodynamic potentials for open systems—Grand Function, Guggenheim Function, Hill Function, and Ray Function—which greatly assist in the transition from thermodynamics to statistical mechanics.

Data and references were updated when appropriate.

No book can be written without the advice of others. It is a great pleasure to acknowledge the assistance of Henry J Graben, David L Hogenboom, Charles Kaufman, J M Marcano, Mark McKenna, Richmond B McQuistan, Sue Nicholls (of Keyword Publishing Services), Dorn W Peterson, George Rainey, John Ray, James E Rutledge, Glenn Schmieg, Dale Snider, Leslie Spanel, and Anna Topal.

Richard H Dittman

NOTATION

CAPITAL ITALIC		LOWER-CASE ITALIC	
A	Helmholtz function; first virial coefficient; area	a	Molar Helmholtz function; a dimension
B	Bulk modulus; second virial coefficient; chemical constituent	b	A dimension; a constant
C	Heat capacity; third virial coefficient; critical point	c	Molar or specific heat capacity; number of chemical constituents; thermocouple coefficients; speed of light
		c'	Components
D	A constant	d	Exact differential
E	Electrical field, ionization potential	e	Base of natural logarithms; equilibrium
F	Force; Faraday's constant	f	Final state; variance; function
G	Gibbs function	g	Molar Gibbs function; acceleration of gravity
		g	Degeneracy
H	Enthalpy; irradiance	h	Molar enthalpy; convection coefficient; Planck's constant
I	Irreversible engine; current	i	Initial state
J	Massieu function; grad function	j	Valence; summation index
K	Thermal conductivity; equilibrium constant	k	Hooke's constant; Boltzmann's constant
L	Length; logarithmic	l	Separation
M	Molar mass	m	Mass of a particle
N	Number of molecules	n	Number of moles; quantum number
P	Pressure	p	Partial pressure; linear momentum

(Contd.)

Q Heat
R Molar gas constant; reversible Carnot engine; electric resistance; Ray function
S Entropy
T Absolute temperature (Kelvin or Rankine)
U Internal energy
V Volume
W Work
X Generalized displacement
Y Generalized force; Young's modulus; Planck function
Z Electric charge; Guggenheim function; partition function

q Molar heat
r Radius; ratio; number of individual reactions
s Molar entropy
t Practical temperature (Celsiu or Fahrenheit); time
u Molar internal energy
v Molar volume
w Molar work; speed of wave c particle
x Space coordinate; mole fraction
y Space coordinate; fraction liquefied
z Space coordinate; number of restricting equations

BOLDFACE CAPITAL ITALICS

$\boldsymbol{B}$ Magnetic induction
$\boldsymbol{D}$ Electric displacement
$\boldsymbol{E}$ Electric field intensity
$\boldsymbol{G}$ Gibbs function of a heterogeneous system
$\boldsymbol{M}$ Magnetization
$\boldsymbol{P}$ Dielectric polarization
$\boldsymbol{S}$ Entropy of a heterogeneous system
$\boldsymbol{V}$ Volume of a heterogeneous system

SPECIAL SYMBOLS

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$\mathcal{E}$ Electromotive force
$\mathcal{F}$ Tension
$\mathcal{H}$ Magnetic field
m Total magnetization
$\mathcal{P}$ Total dielectric polarization
$\mathcal{R}$ Radiant exitance

SCRIPT CAPITALS

$\mathcal{B}$ Magnetic induction
Inexact differential
C_C Curie constant
N_A Avogadro's number
R' Electric resistance
U' Overall heat-transfer coefficient

ROMAN SYMBOLS FOR UNITS

atm	atmosphere (pressure)
dyn	dyne
kg	kilogram
m	meter
s	second
A	ampere
A/m	ampere · turn per meter
C	coulomb
Hz	hertz
J	joule
K	kelvin
N	newton
Pa	pascal
T	tesla
V	volt
W	watt

GREEK LETTERS

α	Linear expansivity; critical-point exponent
β	Volume expansivity; critical-point exponent; $1/kT$
Γ	Grüneisen coefficient
γ	Surface tension; ratio of heat capacities; electronic term in heat capacity; critical-point exponent
Δ	Finite difference
δ	Critical-point exponent
ε	Energy of a particle; permittivity; emissivity; degree of reaction or ionization; reduced temperature difference
ς	Riemann zeta function
η	Thermal efficiency; Joule coefficient
Θ	Debye temperature
θ	Empirical temperature; angle
κ	Compressibility
λ	Wavelength; Lagrangian multiplier
μ	Joule-Thomson coefficient; chemical potential
μ_0	Permeability of vacuum
ν	Frequency; molecular density; stoichiometric coefficient
Π	Osmotic pressure
ρ	Mass density
σ	Stefan-Boltzmann constant
τ	Period
ϕ	Function of temperature; angle
φ	Phase
ψ	Function of temperature
Ω	Solid angle; thermodynamic probability; ohm
ω	Angular speed; coefficient of performance

Dedicated
to

Adele C Zemansky

—*Mark W Zemansky*

Maria M Dittman

—*Richard H Dittman*

and

My Parents

—*Amit K Chattopadhyay*