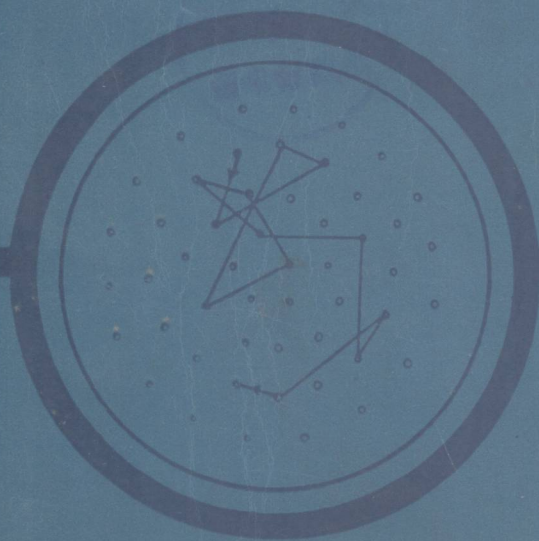


THERMODYNAMICS AND STATISTICAL PHYSICS

SHARMA • SARKAR



Himalaya Publishing House

0414
51
8560550

0414
52
**THERMODYNAMICS
AND
STATISTICAL PHYSICS**

[For B.Sc., B.Sc. (Hon.) & B.E. Students of all Indian Universities]



J.K. Sharma
Ph.D.

K.K. Sarkar
Ph.D.

*Department of Physics
St. John's College
(Agra University)
AGRA*



E8560550



Himalaya Publishing House

“RAMDOOT”, DR. BHALERAU MARG, BOMBAY 400 004.

First Edition—1983

**Published by : Mrs. Meena Pandey, Himalaya Publishing House
Ramdoot', Dr. Bhalerao Marg, (Kelewadi), Girgaon, Bombay-400 004 ; and
Printed at : U.P. Printers, Maujpur, Delhi-110 053.**

**THERMODYNAMICS
AND
STATISTICAL PHYSICS**

Preface

The revolution in Physics, which started with the beginning of this century, can be attributed to the study of Thermodynamics and Statistical Physics. The failure of classical ideas in explaining the spectrum of blackbody radiation and specific heats of solids and gases were mainly responsible for the new ideas of Quantum Physics. Hence a deep understanding of principles of Thermodynamics and Statistical Physics is essential in order to appreciate the modern concepts in Physics.

The authors who have taught the subject to the undergraduate students for a decade have felt the student's difficulty in understanding basic concepts of thermodynamics like 'entropy'. Students at this level are not able to appreciate the beauty and power of statistical methods and this acts as a hinderance in their over-all understanding of Physics. Classics on the subject by Zemansky, Sears and Saha and Shrivastava act as excellent reference books for bright students but an average student finds them difficult to use. This book is an effort to present the concepts of Thermodynamics and Statistical Physics in such a manner as to be understandable to average students of our universities and colleges. The noteworthy features of this book are :

- (a) Fundamental concepts have been explained in a simple and clear manner without a compromise for their exactness.
- (b) The language has been kept straight-forward and simple.
- (c) Large number of solved numerical examples have been given which help the students to develop an understanding of the subject.
- (d) Number of illustrations and tables have been used to supplement the text.
- (e) Many questions and problems at the end of each of the chapters have been selected from examination questions of various Indian universities. This will help the students to prepare accordingly.
- (f) The book covers the syllabus of most of the Indian universities. The chapter on Thermal Conduction has been included with this purpose although it does not

directly form a part of 'Thermodynamics and Statistical Physics'.

- (g) S.I. system of units and symbols has been used throughout the text although some problems are given in C.G.S. units as well.

The authors wish to express gratefulness to their colleagues who have given useful suggestions and discussed some parts of manuscript critically. They are also thankful to Mr. S.K. Joshi of M/S Himalaya Publishing House for his efforts in bringing out the book in present form. The services rendered by M/S U.P. printers are also thankfully acknowledged.

Suggestions and criticism for improvement of the book from fellow teachers and students who will be using this shall be gratefully acknowledged.

Agra

Authors

8560550



Contents

<i>No.</i>	<i>Chapter</i>	<i>Pages</i>
1.	Zeroth Law of Thermodynamics and Temperature	... 1-16
1.1.	Fundamental Concept and Nomenclature	
1.2.	Thermodynamic System and Coordinates	
1.3.	Equation of State	
1.4.	Thermal Equilibrium	
1.5.	Zeroth Law of Thermodynamics ; Concept of Temperature	
1.6.	Empirical Scale of Temperature ; Giauque Scale	
1.7.	Perfect Gas Scale Solved Examples Problems	
2.	First Law of Thermodynamics	... 17-40
2.1.	Concept of Heat	
2.2.	Work and its Sign Convention	
2.3.	Work Through Indicator Diagrams	
2.4.	Thermodynamical Equilibrium and Quasi-Static Processes	
2.5.	Adiabatic Work	
2.6.	Internal Energy Function	
2.7.	First Law of Thermodynamics	
2.8.	First Law and Cyclic Processes	
2.9.	The Two Specific Heats	

10. Various Types of Processes

Solved Examples

Problems

3. Perfect Gases

... 41—59

3.1. Concept of Perfect or Ideal Gases

3.2. Virial Expansion for Real Gases

3.3. Equation of State of a Perfect Gas

3.4. Joule's Experiment and Joule's Law

3.5. The Two Specific Heats of a Perfect Gas

3.6. Quasi-Static Adiabatic Expansion of Perfect Gases

3.7. Work done in Isothermal and Adiabatic Processes in Perfect Gases

3.8. Slopes of Isotherms and Adiabatics in Perfect Gas

Solved Examples

Problems

4. Concept of Real Gases

... 60—96

4.1. Departure From Perfect Gas Laws in Real Gases

4.2. Boyle Temperature and Critical Constants

4.3. Van der Waal's Equation of State for Real Gases

4.4. Nature of Inter-molecular Forces

4.5. Lennard-Jones Potential

4.6. Boyle's Temperature of a Van der Waal's Gas

4.7. Critical Constants of a Van der Waal's Gas

4.8. The Law of Corresponding States

4.9. Departure from Joule's Law in Real Gases

- 4.10. Joule-Thomson Effect (Porus Plug Experiment)
- 4.11. Change of Temperature in Joule-Thomson Effect
- 4.12. Inversion Temperature in Van der Waal's Gas
- 4.13. Inversion Curve
- 4.14. Comparison of Joule, Joule-Thomson and Quasi-Static adiabatic Expansions
Solved Examples
Problems

5. Second Law of Thermodynamics and Entropy

... 97—160

- 5.1. Insufficiency of First Law of Thermodynamics
- 5.2. Perpetual Motions of First and Second Kind
- 5.3. Various Statements of Second Law of Thermodynamics
- 5.4. Heat Engine and Refrigerators
- 5.5. Reversible and Irreversible Processes
- 5.6. Carnot's Engine and Carnot's Cycle
- 5.7. Carnot's Theorem and Corollary
- 5.8. Thermodynamic or Kelvin Scale of Temperature
- 5.9. Equivalence of Kelvin's Thermodynamic and Perfect Gas Scales of Temperature
- 5.10. Latent Heat Equations
- 5.11. Clausius Theorem
- 5.12. Entropy ; a Point Function
- 5.13. Entropy as a Thermodynamic Coordinate
- 5.14. T-S Indicator Diagram
- 5.15. Entropy of Universe in Reversible Processes

- 5.16. Entropy of Universe in Irreversible Processes
- 5.17. Principle of Increase in Entropy]
- 5.18. Physical Significance of Entropy
- 5.19. Entropy as a Direct Proposition of Second Law
- 5.20. Third Law of Thermodynamics ; Nernst Heat Theorem
- 5.21. Calculation of Entropy Change in different Processes
Solved Examples
Problems
- 6. Applications of Laws of Thermodynamics ... 161—202**
 - 6.1. Maxwell's Thermodynamical Relations
 - 6.2. Thermodynamical Potentials
 - 6.3. Maxwell's Equations from Thermodynamical Potentials
 - 6.4. The Two Tds Equations
 - 6.5. Applications to Various Problems
 - 6.6. Clausius Clapeyron's Latent Heat Equation
 - 6.7. The Triple Point ; Thomson's Theorem
 - 6.8. Perfect Gas Equation
 - 6.9. Joule-Thomson Effect
 - 6.10. The Energy Equation
 - 6.11. Ratio of Two Specific Heats
 - 6.12. Difference of Two Specific Heats
 - 6.13. Adiabatic Stretching of a Wire
 - 6.14. Application to Paramagnetic Salts ; Magneto-Caloric Effect
 - 6.15. Application to Surface Films
 - 6.16. Application to Chemical Thermodynamics
Solved Examples
Problems

7. Experimental Applications of Thermodynamics (Production of Low Temperatures)	... 203—226
7.1. Introduction to Cryogenics ; Refrigeration	
7.2. Cooling by Evaporation ; Vapour Compression Refrigerator	
7.3. Cascade or Series Refrigeration	
7.4. Cooling by Adiabatic Expansion ; Air Expansion Machine	
7.5. Cooling by Joule-Thomson Throttling Process ; Hampson's and Linde's Regenerative Cooling Machine	
7.6. Liquefaction of Air, Hydrogen and Helium	
7.7. Liquefaction of Helium ; Production of Temperatures below 4 K	
7.8. Cooling by Adiabatic Demagnetization ; an Approach to Absolute Zero Solved Examples Problems	
8. Thermal Conduction in Solids	... 227—254
8.1. Introduction	
8.2. Some Important Concepts in Heat Conduction	
8.3. General Equation of Heat Conduction	
8.4. Heat Conduction Through a System of Plane Slabs	
8.5. Analysis of Heat Conduction Through a Rod	
8.6. Comparison of Thermal Conductivities of Metals ; Ingen Hausz Experiment	
8.7. Determination of Absolute Conductivity of a Metal ; Forbe's Method	

8.8.	Heat Conduction Through Axially Heated Cylindrical Shell	
8.9.	Conduction Through Spherical Shell Heated at Centre	
8.10.	Freezing of Ice on Surface of Ponds	
8.11.	Conduction of Heat Through an Insulated Rod Heated Sinusoidally at one End Solved Examples Problems	
9.	Elements of Classical Statistics	... 225—278
9.1.	Introduction	
9.2.	Probability	
9.3.	Probability of Particular Distribution of N Particles in Two Boxes	
9.4.	Probability Distributions	
9.5.	Definition of Some Important Terms	
9.6.	Basic Postulate About Equal a Priori Probability	
9.7.	General Procedure of Statistical Approach	
9.8.	Thermodynamical Probability	
9.9.	Systems in Thermal Equilibrium	
9.10.	Probability and Entropy	
9.11.	Boltzmann Canonical Distribution	
9.12.	Partition Function	
9.13.	Mean Energy of Harmonic Oscillator Problems	
10.	Kinetic Theory of Gases	... 279—301
10.1.	Introduction	
10.2.	Microscopic View of An Ideal Gas	
10.3.	Degrees of Freedom	
10.4.	Law of Equipartition of Energy	
10.5.	Distribution of Velocities in Monoatomic Ideal Gas	

- 10.6. Distribution of Molecular Speeds in Monoatomic Gas
- 10.7. Mean Speed and Root Mean Square Speed
- 10.8. Energy-wise Distribution of Molecules
- 10.9. Expressions for Most Probable Energy E_{peak} , Average Energy and P_{peak} for Maxwellian Distribution
- 10.10. Pressure Exerted by a Gas
- 10.11. Kinetic Interpretation of Temperature
Solved Examples
Problems

11. Transport Phenomenon in Gases ... 302—315

- 11.1. Introduction
- 11.2. Molecular Dimensions and Collisions
- 11.3. Mean Free Path and Mean Free Time
- 11.4. Probability of a Particle Travelling Distance x Without Collision
- 11.5. Viscosity in Gases
- 11.6. Thermal Conduction in Gases
- 11.7. Diffusion in Gases
Solved Examples
Problems

12. Thermal Radiation ... 316—353

- 12.1. Introduction
- 12.2. Definitions of Some Important Physical Quantities
- 12.3. Black Body
- 12.4. Prevost's Theory of Exchanges of Radiations
- 12.5. Isothermal Enclosure as a Black Body

- 12.6. Kirchoff's Law
- 12.7. Pressure of Radiation and Energy Density
- 12.8. Relation Between Emissive Power E and Energy Density u of a Black Body
- 12.9. Stefan-Boltzmann Law
- 12.10. Proof of Stefan-Boltzmann Law From Thermodynamics
- 12.11. Spectrum of Black Body Radiation
- 12.12. Wein's Displacement Law
- 12.13. Deduction of Wein's Law
- 12.14. Various Laws For Energy Distribution in Black Body Spectrum
- 12.15. Radiation Pyrometry
- 12.16. Total Radiation Type ; Fery's Pyrometer
- 12.17. Optical or Spectral Type Pyrometers
- 12.18. Solar Constant and Temperature of Sun
Solved Examples
Problems.

13. Quantum Theory of Radiation ... 354—367

- 13.1. Quantum Concept
- 13.2. Counting Number of Modes of Vibration in Frequency Range ν to $\nu + d\nu$
- 13.3. Rayleigh-Jean's Law
- 13.4. Planck's Distribution Formula
- 13.5. Relation of Planck's Law with Wein's and Rayleigh-Jean's Law
- 13.6. Relation Between Planck's Law and Stefan's Law
Solved Examples
Problems

14. Specific Heat of Solids and Gases ... 368—391

14.1. Introduction

14.2. Specific Heat of Solids—Dulong and Petit's Law

14.3. Deduction of Dulong and Petit's Law from Classical Statistics

14.4. Temperature Variation of Specific Heat

14.5. Einstein's Theory of Specific Heat of Solids

14.6. Debye's Theory of Specific Heat
Solved Examples

14.7. Specific Heat of Gases

14.8. Temperature Variation of Specific Heat of Diatomic Gases

14.9. Quantization of Various Contributions to Energy of a Diatomic Molecule

14.10. Specific Heat of Diatomic Gases (Quantum Theory)
Solved Examples
Problems

Appendix A—Some useful definite integrals

Appendix B—Physical constants and conversion factors

Answers to Numerical Problems

Zeroth Law of Thermodynamics and Temperature

1.1. Fundamental Concepts and Nomenclature

Thermodynamics is one of the cardinal branches of Physics which is a perfect mathematical science describing the inter-relationship between heat and any diverse form of energy *viz.* mechanical, electrical, magnetic, chemical etc. The basic concept starts with the transformation of heat into mechanical work through any bulk matter. It has innumerable applications in Physics, Chemistry and Engineering Sciences.

It has become quite an established theory now that a bulk matter constitutes of molecules and atoms which themselves are made up of protons, neutrons, electrons etc. Atomic and Nuclear Physics are other two well developed branches of Physics which supply considerable knowledge about the interactions between these fundamental particles. The mathematics of such interactions makes it possible to analyse the properties of bulk matter like thermal expansion, elasticity, specific heat etc. in terms of the detailed structure of matter. However, the study of thermodynamics takes no account of the atomic constitution, though the atomic interactions, the interactions between electrons, protons, neutrons etc., are stronger than that between two or more molecules. This is because the descriptions of most of the bulk properties of matter do not need to consider the internal changes occurring within the molecules or atoms. Thus in order to understand the thermodynamical properties of bulk matter, the inter-molecular interactions will be taken as sufficient. In the future text of the book, however, some special treatment may use the interactions between electrons, protons, neutrons etc.

For all practical purposes, now onward a bulk system will be thermodynamically called a *macroscopic system* while the molecules, which form a "macro" body will be called the *microscopic system*. The microscopic interactions will interpret the properties of macroscopic system. The validity of the names

'macro' and 'micro' is quite evident in the sense that the number of molecules in one gram mole of any substance is 6.06×10^{23} (Avogadro's number). This obviously indicates that 2 gm of hydrogen or 32 gm of oxygen have 6.06×10^{23} molecules. Volume-wise, even a gas at normal temperature and pressure, which has smallest number of molecules per unit volume as compared to liquids and solids, will have approximately 3×10^{25} molecules in one cubic metre (one gm mole of a gas occupy $2.2 \times 10^{-2} \text{ m}^3$ at normal temperature and pressure). Such a huge number of molecules in a small volume or mass of gas proves the validity of terms 'micro' and 'macro' for molecules and total bulk respectively.

The internal changes occurring inside a molecule give rise to the *rotational, vibrational and electronic* energies in discrete steps. The state of a molecule with the lowest possible energy is called the *ground state* and with respect to the ground state, all other states are called *excited states*. These are the *internal energy states of a molecule*. However, molecules in a bulk matter will always have *potential and kinetic energies* due to intermolecular interactions and their own translational motions respectively. In a well defined coordinate frame of reference the position coordinate gives the potential energy and momenta coordinates give the kinetic energy. Since the position and momenta coordinates give the external description of the molecules, the potential and kinetic energies are called *external energies of molecules*. Our present context will not deal, in general, with the internal energy states of the molecules as the molecules themselves are defined as 'micro' system.

We describe the relative microscopic and macroscopic motions of a bulk matter of mass M in Fig. 1.1. Let us consider a frame of reference XYZ fixed in laboratory in which the mass M is moving with a uniform velocity

\vec{V} . One can fix another frame of reference xyz with its origin at the centre of mass of that body and the velocities of the molecules inside the body may be referred to in this c.m. frame (c.m. stands for centre of mass).

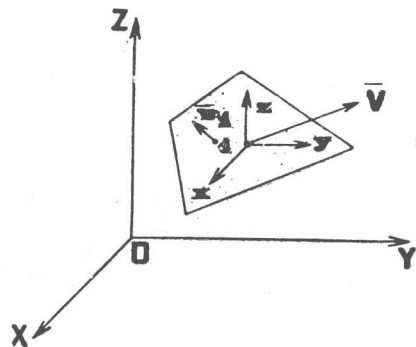


Fig. 1.1. Relative microscopic and macroscopic movements.

Let v_i be the velocity of i th molecule in c.m. frame. C.m. frame

itself has a relative velocity \vec{V} with respect to lab frame (Lab stands for laboratory). Since the relative velocity of the entire body with respect to c.m. frame is zero, the total momentum is zero, i.e.,

$$\sum_i m_i v_i = 0 \quad \dots(1.1)$$