HEAT
and
THERMODYNAMICS

AN INTERMEDIATE TEXTBOOK FOR STUDENTS OF
PHYSICS, CHEMISTRY, AND ENGINEERING

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SECOND EDITION
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HEAT AND THERMODYNAMICS

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Dedicated to

ADELE C. ZEMANSKY

PREFACE TO THE SECOND EDITION

The scope, limitations, and unified point of view of the original edition of this book have been maintained in the second edition. Some of the old material has been rewritten in order to bring it up to date or to make it more rigorous, and some new material has been added. Among the topics that have been discussed more completely are the temperature concept, the first law of thermodynamics, the equivalence of the Kelvin-Planck and Clausius statements of the second law, the phase rule, and various experimental methods. The new topics include convection, entropy and nonequilibrium states, second-order phase transitions, superconductivity, heat capacity of reacting gas mixtures, and Le Châtelier's principle. There are many new problems.

In this revision, the author has been aided by the suggestions and criticisms of various teachers throughout the country. Chief among these is Professor H. C. Wolfe, whose keen critical judgment has been of inestimable value. The author has also profited from three new books on thermodynamics that have recently appeared, *viz.*, those by Epstein, Fermi, and Keenan, and is grateful to Professor Keenan for permission to use some of his problems in the chapter on engineering applications of thermodynamics.

M. W. Z.

NEW YORK, N. Y.
July, 1943.

PREFACE TO THE FIRST EDITION

This book is an amplification of notes that have been used by the author and his colleagues for the past five years in connection with an elective course in heat and thermodynamics for which the only prerequisites were a course in general college physics and one in college calculus. It is designed as an intermediate textbook to supply the needs of students who are in the first stage of preparation for a career in theoretical physics, theoretical chemistry, or engineering.

The first ten chapters deal with the fundamental ideas of heat, reversibility, entropy, etc., in a manner which strives at a compromise between rigor and simplicity. The remaining 9 chapters deal with physical, chemical, and engineering applications in sufficient detail to show how the general principles are applied to specific cases. An attempt has been made to reduce the number of occasions in which the student is asked to refer back to a previous equation. This has entailed some repetition but is, in the author's opinion, pedagogically worth while. Mathematical theorems beyond the scope of a first course in calculus are given and proved in the body of the text at the points where they are needed. Methods of measurement are explained and experimental results are tabulated in all cases where it is desired to point out a significant relationship. Problems are listed at the end of each chapter.

The properties of chemical, electric, and magnetic systems are introduced in the beginning of the book and are used in general discussions instead of being reserved for special treatment at the end. Diagrams of thermodynamic surfaces showing the properties of pure substances are used to a greater extent than in most books of this kind. Chemical reactions are discussed in terms of the important variable, the "degree of reaction," in a manner similar to that of de Donder. With the aid of this variable, the importance of the affinity of a reaction is emphasized. Recent advances, such as the production of low temperatures by adiabatic demagnetization, the measurement of these temperatures on the Kelvin scale, modern methods of measurement of vapor-pressure constants, Bridgman's treatment of thermoelectric phenomena, etc., are discussed fully. By the use of script capitals to denote intensive variables or generalized forces, it has been found possible to make the notation fairly consistent with modern chemical and engineering practice, while retaining most of the well-established physical symbols.

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The author believes that the study of molecular physics embodied in statistical mechanics and kinetic theory should not run parallel with but should follow a course in thermodynamics, in order that the power and limitations of the macroscopic point of view may be clearly understood and not confused with those of the microscopic point of view. For this reason, and also because of the limited mathematical training of those for whom this book is intended, statistical mechanics and kinetic theory are not included. No mention of the Nernst heat theorem has been made for two reasons: first, the background of chemistry and statistical mechanics necessary for a real comprehension of the theorem is lacking; second, all the thermodynamic applications that fall within the scope of this book can be made without the use of the theorem. The axiomatic treatment of the second law of Caratheodory and Ehrenfest is omitted because of the mathematical difficulties inherent in the subject.

A list of the books which have been consulted and from which valuable material has been obtained is given on page 379. The author would like to make particular mention of the splendid treatises of Roberts, Planck, Lewis and Randall, Kiefer and Stuart, and Bridgman.

It is a particular pleasure for the author to acknowledge his indebtedness for the help given him by his colleagues, Professor Henry Semat, Professor Charles A. Marlies, Dr. Lewis Balamuth, and Dr. Hugh C. Wolfe, who read the manuscript and suggested many important changes. Particular thanks are due to Adele C. Zemansky for typing the manuscript and helping in the correction of proof.

M. W. Z.

New York, N. Y.,
August, 1937.

NOTATION

Capital Italics		Lower-case Italics	
A	Helmholtz function, area, first virial coefficient	a	Molar or specific Helmholtz function
B	Bulk modulus, second virial coefficient, magnetic induction	b	Stefan-Boltzmann constant
C	Heat capacity, Curie constant	c	Molar or specific heat capacity, number of constituents
D	Debye function	d	Exact differential sign
E	Unavailable energy, ionization potential	e	Napierian logarithmic base, emissivity
G	Gibbs function	g	Molar or specific Gibbs function, acceleration of gravity
H	Enthalpy, irradiancy	h	Molar or specific enthalpy, convection coefficient
I	Magnetization, electric current	i	Molar or specific magnetization, vapor pressure constant
J	Mechanical equivalent of heat	j	Valence
K	Equilibrium constant	k	Compressibility, thermal conductivity
L	Length, latent heat	l	Molar or specific latent heat
M	Molecular weight	m	Mass
N	Avogadro's number	n	Number of moles
P	Total pressure	p	Partial pressure
Q	Heat	q	Molar or specific heat
R	Universal gas constant, electrical resistance	r	Radius, number of independent reactions
S	Entropy	s	Molar or specific entropy
T	Kelvin or Rankine temperature	t	Centigrade or Fahrenheit temperature
U	Internal energy	u	Molar or specific internal energy, energy density
V	Volume	v	Molar or specific volume

W	Work
X	Generalized displacement
Y	Young's modulus
Z	Electric charge

Script Capitals

$\mathcal{E}$	Electromotive force
$\mathcal{T}$	Tension
$\mathcal{H}$	Magnetic field intensity
$\mathcal{R}$	Radiancy
$\mathcal{S}$	Surface tension
$\mathcal{V}$	Velocity
$\mathcal{Y}$	Generalized force

Boldface Capitals

$\mathbf{F}$	Faraday's constant
$\mathbf{G}$	Gibbs function of a heterogeneous system
$\mathbf{V}$	Volume of a heterogeneous system
$\mathbf{S}$	Entropy of a heterogeneous system

Special Symbols

đ	Inexact differential sign
ln	Natural logarithm
log	Common logarithm
T^*	Magnetic temperature

w	Molar or specific work
x	Space coordinate, mole fraction, quality
y	Space coordinate, fraction liquefied
z	Number of independent restricting equations

Greek Letters

α	Coefficient of linear expansion
β	Coefficient of volume expansion
γ	Ratio of heat capacities
δ	Variance
ϵ	Degree of reaction, electronic charge, dielectric coefficient
η	Efficiency
θ	Absolute temperature
Θ	Debye characteristic temperature
λ	Wave length
μ	Joule-Kelvin coefficient, chemical potential
ν	Stoichiometric coefficient, frequency
π	Peltier coefficient
ρ	Density
σ	Thomson coefficient, Stefan-Boltzmann constant
τ	Time, period
ϕ	A special function of the temperature
φ	Number of phases
Δ	Finite difference
ω	Coefficient of performance

CONTENTS

PAGE

PREFACE TO THE SECOND EDITION vii

PREFACE TO THE FIRST EDITION ix

NOTATION xiii

CHAPTER I

TEMPERATURE 1

CHAPTER II

THERMODYNAMIC SYSTEMS 22

CHAPTER III

WORK 39

CHAPTER IV

✓THE FIRST LAW OF THERMODYNAMICS 53

CHAPTER V

HEAT 63

CHAPTER VI

✓IDEAL GASES 94

CHAPTER VII

✓THE SECOND LAW OF THERMODYNAMICS 118

CHAPTER VIII

REVERSIBILITY AND IRREVERSIBILITY 131

CHAPTER IX

THE CARNOT CYCLE AND THE KELVIN TEMPERATURE SCALE 137

CHAPTER X

ENTROPY 149

CHAPTER XI

PROPERTIES OR PURE SUBSTANCES 174

PAGE

CHAPTER XII

THE STEAM ENGINE AND THE REFRIGERATOR 200

CHAPTER XIII

APPLICATIONS OF THERMODYNAMICS TO PURE SUBSTANCES. 219

CHAPTER XIV

APPLICATIONS OF THERMODYNAMICS TO SPECIAL SYSTEMS 249

CHAPTER XV

CHANGE OF PHASE 284

CHAPTER XVI

MIXTURE OF INERT IDEAL GASES. 307

CHAPTER XVII

✓CHEMICAL THERMODYNAMICS. 316

CHAPTER XVIII

✓IDEAL GAS REACTIONS 331

CHAPTER XIX

HETEROGENEOUS SYSTEMS. 354

BIBLIOGRAPHY. 379

INDEX 381

ANSWERS TO PROBLEMS. 389

HEAT AND THERMODYNAMICS

CHAPTER I

TEMPERATURE

1.1. Macroscopic Point of View.—The study of any special branch of physics starts 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 the 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 that will be helpful in discussing 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* point of view and the *microscopic* point of view.

Let us take as a system the contents of a cylinder of an automobile engine. A chemical analysis would show a mixture of gasoline vapor and air before explosion, and after the mixture has 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 attached to the piston as it moves in the cylinder. 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. This quantity is the *temperature;* as we shall see, 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 tem-

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perature. 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. Only a few coordinates are needed for a macroscopic description.
3. Macroscopic coordinates are suggested more or less directly by our sense perceptions.
4. Macroscopic coordinates 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. The student will recognize that, in elementary physics, the macroscopic point of view is adopted in most cases, although no consistent attempt is made to adopt it at all times. To understand clearly the distinction between the macroscopic point of view and the microscopic, let us give a simple microscopic description of a gas in a containing vessel.

1.2. Microscopic Point of View.—We shall assume that a 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, six numbers are required. A microscopic description of the state of the gas consists of the specification of these six numbers for each of the N molecules. This may be accomplished in a manner that suggests Huygens' method in the elementary treatment of diffraction. The student will recall that, in the study of simple problems in diffraction, a wave front is subdivided into small regions called Fresnel zones and that the effect of the whole wave front at some point in space is obtained by considering the effect of each zone separately. In an analogous manner, we imagine a six-dimensional space called a *phase space* whose coordinates are x, y, z, v_x, v_y, v_z. Suppose the phase space is divided into a large number of small regions called *cells.* Each cell in the phase space corresponds to a limited region of position and velocity and therefore to a certain average energy.

A simple microscopic description of the gas is given by stating that

1. There are n_1 molecules in cell 1 with average energy e_1.
2. There are n_2 molecules in cell 2 with average energy e_2.

. . .
. . .
. . .

The total number of molecules is evidently equal to

$$N = n_1 + n_2 + \cdots ,$$

and the total energy U is given by

$$U = n_1 e_1 + n_2 e_2 + \cdots .$$

This type of description is used in an important branch of physics called *statistical mechanics.* It is not necessary to pursue the matter further to understand that a microscopic description involves the following characteristics:

1. Assumptions are made concerning the structure of matter; *i.e.*, 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 vs. 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 agree in the end. 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 physicists had reason to believe in the existence of molecular impacts. If the molecular theory is changed or discarded at some time in the future, the concept of pressure will still remain and will still mean the same thing to all normal human beings. 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 the macroscopic point of view.

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 physics. For example, in dealing with the mechanics of a rigid body, the macroscopic point of view is adopted 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. Position and time and a combination of both, such as velocity, constitute some of the macroscopic quantities used in mechanics and are called *mechanical coordinates.* The mechanical coordinates serve to determine the potential and the kinetic energy of the rigid body with reference to the coordinate axes, *i.e.*, the kinetic and the potential energy of the body as a whole. These two types of energy constitute the *external,* or *mechanical, energy* of the rigid body. It is the purpose of mechanics to find such relations between the position coordinates and the time as are consistent with Newton's laws of motion.

In thermodynamics, however, the attention is directed to the *interior* of a system. A macroscopic point of view is adopted, but only those macroscopic quantities are considered which have a bearing on the internal state of a system. It is the function of experiment to determine the quantities that are necessary and sufficient for such a purpose. *Macroscopic quantities having a bearing on the internal state of a system are called thermodynamic coordinates.* Such coordinates serve to determine the *internal energy* of a system. It is the purpose of thermodynamics to find general relations among the thermodynamic coordinates that are consistent with two fundamental laws known, respectively, as the first and second laws of thermodynamics.

A system that may be described in terms of thermodynamic coordinates is called a *thermodynamic system.* In engineering the important thermodynamic systems are a gas, such as air; a vapor, such as steam; a mixture, such as gasoline vapor and air; and a vapor in contact with its liquid, such as liquid and vaporized ammonia. Chemical thermodynamics deals with the above systems and, in addition, with solids, surface films, and electric cells. Physical thermodynamics includes, in addition to the above, such systems as stretched wires, electric capacitors, thermocouples, and magnetic substances.

1.5. Thermal Equilibrium.—We have seen that a macroscopic description of a gaseous mixture may be given by specifying such quantities as the composition, the mass, the pressure, and the volume. Experiment shows that, for a given composition and for a constant mass, many different values of pressure and volume are possible. If the pressure is kept constant, the volume may vary over a wide range of values, and vice versa. In other words, the pressure and the volume are independent coordinates. Similarly, experiment shows that, for a wire of constant mass, the tension and the length are independent coordinates, whereas, in the case of a surface film, the surface tension and the area may be varied independently. Some systems that, at first sight, seem quite complicated, such as an electric cell with two different electrodes and an electrolyte, may still be described with the aid of only two independent coordinates. On the other hand, some systems composed of a number of homogeneous parts require the specification of two independent coordinates for each homogeneous part. Details of various thermodynamic systems and their thermodynamic coordinates will be given in Chap. II. For the present, to simplify our discussion, we shall deal only with systems of constant mass and composition, each requiring *only one pair* of independent coordinates for its description. This involves no essential loss of generality and results in a considerable saving of words. In referring to any nonspecified system, we shall use the symbols Y and X for the pair of independent coordinates.

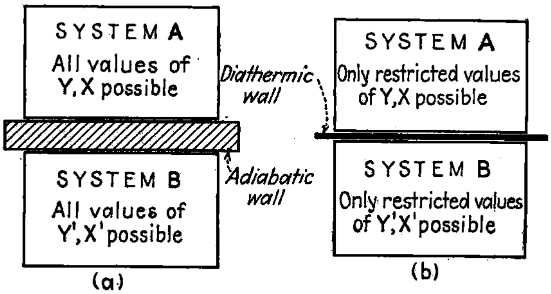
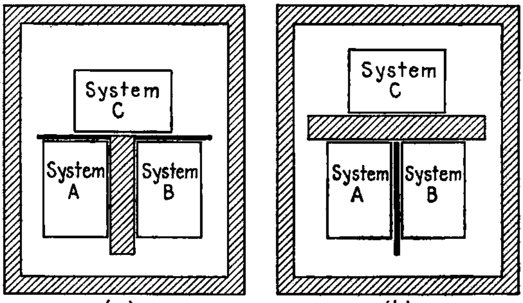

SYSTEM A
All values of Y,X possible
Diathermic wall
SYSTEM A
Only restricted values of Y,X possible
SYSTEM B
All values of Y',X' possible
Adiabatic wall
SYSTEM B
Only restricted values of Y',X' possible
(a)
(b)

FIG. 1.1.—Properties of adiabatic and diathermic walls.

A state of a system in which Y and X have definite values which remain constant so long as the external conditions are unchanged is called an *equilibrium* state. Experiment shows that the existence of an equilibrium state in one system depends on the proximity of other systems and on the nature of the wall separating them. Walls are said to be either adiabatic or diathermic. If a wall is *adiabatic* (see Fig. 1.1*a*), a state Y, X for system A and Y', X' for system B may coexist as equilibrium states for *any* attainable values of the four quantities, provided only that the wall is able to withstand the stress associated with the difference between the two sets of coordinates. Thick layers of wood, asbestos, felt, etc., are good experimental approximations to adiabatic walls. If the two systems are separated by a *diathermic* wall (see Fig. 1.1*b*), the values of Y, X and Y', X' will change spontaneously until an equilibrium state of the combined system is attained. The two systems are then said to be in *thermal equilibrium* with each other. The commonest diathermic wall is a thin metallic sheet. *Thermal equilibrium is the state achieved by two (or more) systems, characterized by restricted* *values of the coordinates of the systems, after they have been in communication with one another through a diathermic wall.*

Imagine two systems A and B separated from each other by an adiabatic wall but each in contact with a third system C through diathermic walls, the whole assembly being surrounded by an adiabatic wall as shown in Fig. 1.2*a*. Experiment shows that the two systems will come to thermal equilibrium with the third and that no further change will occur if the adiabatic wall separating A and B is then replaced by a diathermic wall (Fig. 1.2*b*). If, instead of allowing both systems A and B to come to equilibrium with C at the same time, we first have equilibrium between A and C and then equilibrium between B and C (the state of system C being the same in both cases), then, when A and B are brought into communication through a diathermic wall, they will be found to be in thermal equilibrium. We shall use the expression "two systems are in thermal equilibrium" to mean that the two systems are in states such that, if the two *were* connected through a diathermic wall, the combined system *would be* in thermal equilibrium.



(a)
If A and B are each in thermal equilibrium with C, then

(b)
A and B are in thermal equilibrium with each other

FIG. 1.2.—The zeroth law of thermodynamics. (Adiabatic walls are designated by cross shading, diathermic walls by heavy lines.)

These experimental facts may then be stated concisely in the following form: *Two systems in thermal equilibrium with a third are in thermal equilibrium with each other.* Following R. H. Fowler, we shall call this postulate the *zeroth law of thermodynamics.*

1.6. Temperature Concept.—Consider a system A in the state Y_1, X_1 in thermal equilibrium with a system B in the state Y_1', X_1'. If system A is removed and its state changed, there will be found another state Y_2, X_2 in which it is in thermal equilibrium with the *original* state Y_1', X_1' of system B. Experiment shows that there exists a whole set of states $Y_1, X_1; Y_2, X_2; Y_3, X_3; \ldots$ every one of which is in thermal equilibrium with this *same* state Y_1', X_1' of system B and which, by the zeroth law, are in thermal equilibrium with one another. We shall suppose that *all* such states, when plotted on a Y-X diagram, lie on a curve such as I in Fig. 1.3, which we shall call an *isotherm*. *An isotherm is the locus of all points representing states at which a system is in thermal equilibrium with one state of another system.* We make no assumption as to the continuity of the isotherm, although experiments on simple systems indicate usually that at least a portion of an isotherm is a continuous curve.

Similarly, with regard to system B, we find a set of states Y'_1, X'_1; Y'_2, X'_2; . . . all of which are in thermal equilibrium with one state (Y_1, X_1) of system A, and therefore in thermal equilibrium with one another. These states are plotted on the Y'-X' diagram of Fig. 1.3 and lie on the isotherm I′. From the zeroth law, it follows that all the states on isotherm I of system A are in thermal equilibrium with all the states on isotherm I′ of system B. We shall call curves I and I′ *corresponding isotherms* of the two systems.

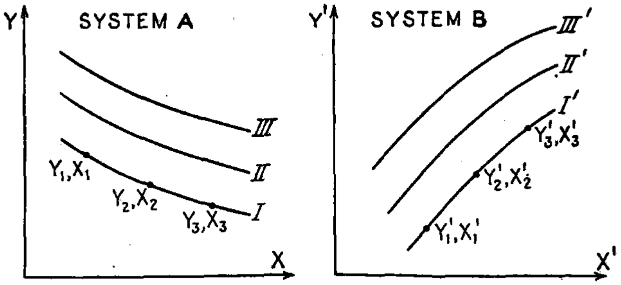


FIG. 1.3.—Isotherms of two different systems.

If the experiments outlined above are repeated with different starting conditions, another set of states of system A lying on curve II may be found, every one of which is in thermal equilibrium with every state of system B lying on curve II′. In this way, a family of isotherms, I, II, III, etc., of system A and a corresponding family I′, II′, III′, etc., of system B may be found. Furthermore, by repeated applications of the zeroth law, corresponding isotherms of still other systems C, D, etc., may be obtained.

All states of corresponding isotherms of all systems have something in common, *viz.*, that they are in thermal equilibrium with one another. The systems themselves, in these states, may be said to possess a property that ensures their being in thermal equilibrium with one another. We call this property *temperature*. *The temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems.*

The temperature of all systems in thermal equilibrium may be represented by a number. The establishment of a temperature scale is merely the adoption of a set of rules for assigning one number to one

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