Thermo-statics and Thermo-dynamics

MYRON TRIBUS

THERMOSTATICS

AND

THERMODYNAMICS

An Introduction to Energy, Information and
States of Matter, with Engineering Applications

by

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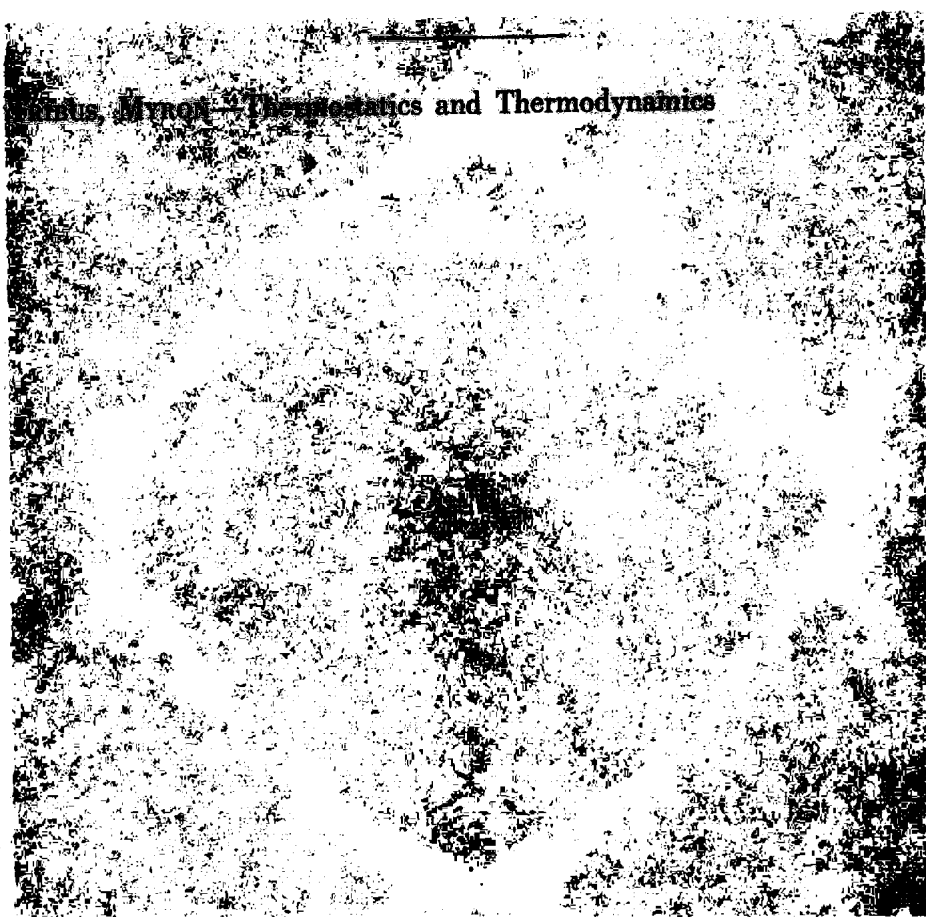
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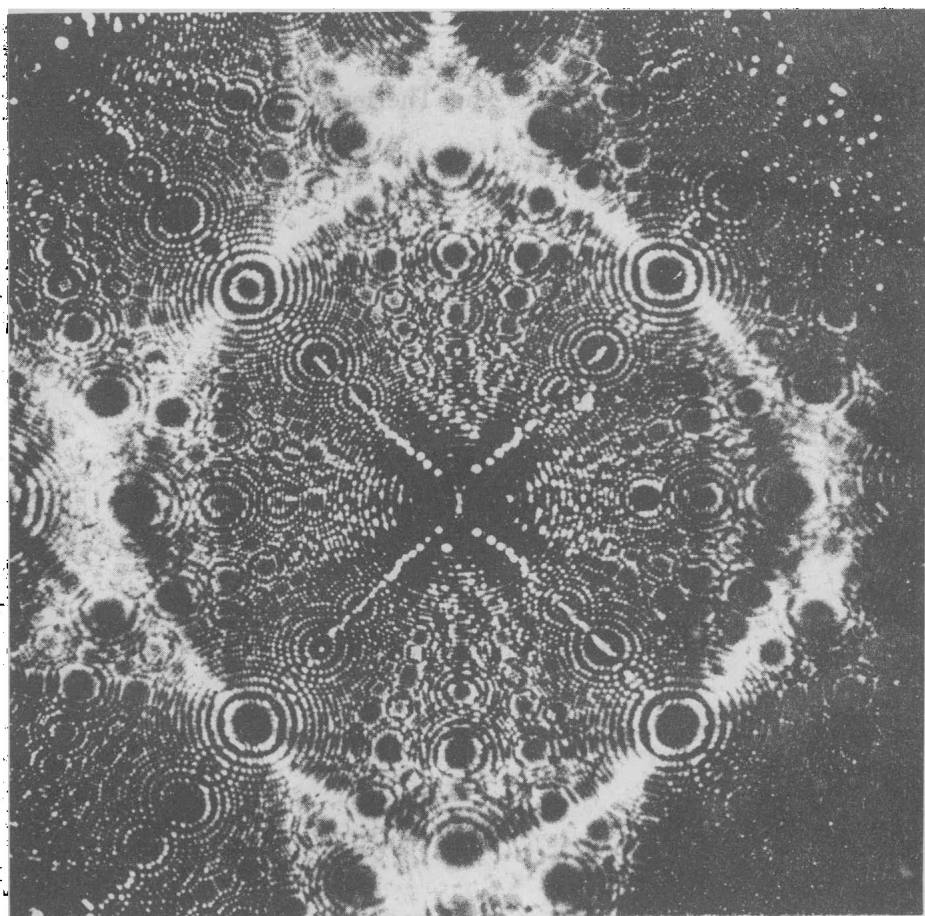
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ATOMS ARE REAL

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Tribus, Myron — Thermostatics and Thermodynamics

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PREFACE

Ever since Rudolf Clausius wrote his book *Abhandlungen über die mechanische Wärmetheorie* (Brunswick, 1864–67),[1] the pattern of engineering textbooks in thermodynamics has remained relatively unchanged. There have been shifts in emphasis as interests have varied from the steam engines of a century ago, but, despite the changes, one can read Clausius' book today and not find it out of date. The point of view that treats matter as a continuum and the first and second principles as axioms, and proclaims that the detailed nature of particle behavior is of no interest—this point of view is the common thread that ties together the engineering texts of today and the books of nearly a century ago.

The mainstream of physics and chemistry has been subtly moving away from this point of view. The undergraduate texts in science still start with the caloric theory and discuss its decline in favor of the mechanical theory. Energy is introduced as a quantity that depends on the macroscopic state of a body with no mention of its statistical character. When entropy is introduced to the students, a qualitative treatment of the relationship between probability and entropy is also often introduced in modern books as a sort of "crutch" to help them. As soon as possible, however, these pretenses are dropped and the students in chemistry and physics are then introduced to the "true" nature of thermodynamics, viz. statistical mechanics. In this subject, the mysteries of macroscopic thermodynamics are "cleared up," though they are replaced by more formidable ones. "We are still confused, but on a higher level," as the saying goes. Meanwhile the students of engineering remain, a century removed, the disciples of Rudolf Clausius. The statistical treatment has been considered suitable for engineers only at the graduate level.

The reasons for the conservatism in engineering instruction are simple. Before one can do much with statistical mechanics, a certain amount of discussion about such abstract ideas as phase space, ergodic system and cells in phase space has heretofore been considered to be required for a rigorous development. Before one could get to the practical calculations that interest an engineer, it has been necessary to master a formidable number of specialized mathematical tools. The number of *systems* problems (as opposed to *materials* problems) that can be solved via statistical mechanics is limited, and even though the statistical treatment clearly illuminates and defines the macroscopic, classical methods, *it simply has not been worth the time to introduce the statistical methods only to make the macroscopic methods more palatable.* The macroscopic methods remain the principal tool of the engineer, and since

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[1] Clausius, R., *The Mechanical Theory of Heat,* transl. by Hirst, Van Voorst, London, 1867.

they could be taught without recourse to statistics, they have been so taught.

In 1957, E. T. Jaynes of Stanford University published a remarkable paper. Ever since 1948, the work of Claude Shannon of the Bell Telephone Laboratories on the mathematical theory of communication had shown a formal relation between information theory and thermodynamics. Jaynes, in his paper "Information Theory and Statistical Mechanics," [2] showed that, if one took the ideas of information theory as primitive and more basic than thermodynamics, all of the formulae of statistical mechanics could easily be derived. It follows that the "laws" of thermodynamics can also easily be derived.

The mathematical tools and the abstract ideas required by Jaynes' methods are less demanding than are those required for, say, Carathéodory's treatment of macroscopic thermodynamics, an approach seriously advocated by some authors. The mathematical methods required for Jaynes' approach are of more general applicability in engineering than are those employed in macroscopic thermodynamics.

It seemed useful, therefore, to attempt the writing of a textbook for undergraduate students in engineering, presenting thermostatics and thermodynamics from Jaynes' point of view. As the work progressed, it became evident that many important advantages were likely to occur, not the least of which is the treatment of reversible and irreversible phenomena in a unified way. The reader will have to judge whether this treatment now makes the effort worth while.

The author envies those many writers of text in macroscopic thermodynamics, who have had nearly a century of authors by whom to be guided. Where the macroscopic view predominates, he has not hesitated to do likewise.

"Research," said one wag, "is reading *more* than *one* book." The author has "researched" the textbook field and has been influenced by what he has read. He does not claim to have read the 18,145 separate references to the literature given by Partington,[3] and alongside the obvious erudition of such a man he feels that the quotation from Tolman [4] given by Partington may well apply: "minor scientists who hurry into print with the complicated applications of theories they do not understand. . . ."

In the field of statistical mechanics, the author has been influenced most by the writings of Schrödinger [5]; in classical thermodynamics, by the book of Lewis and Randall (as taught by W. F. Giauque, who may surely be discharged of any responsibility for what is in this book); and, above all, by the writings of Josiah Willard Gibbs. In the consideration of irreversible phenomena, the little booklet by K. G. Denbigh [6] was most helpful.

[2] *Phys. Rev.,* Vol. 106, No. 4, pp. 620–630, May 1957; Vol. 108, No. 2, pp. 171–190, Oct. 1957.

[3] Partington, J. R., *An Advanced Treatise on Physical Chemistry,* Longmans Green & Co., London, 1949.

[4] Tolman, R. C., *J. Am. Chem. Soc.,* Vol. 52, p. 3742 (1930).

[5] Schrödinger, E., *Statistical Thermodynamics,* Cambridge University Press, 1946.

[6] Denbigh, K. G., *Thermodynamics of the Steady State,* Methuen, London, 1950.

Professor George Tunell of our Geology Department has tried to keep my eyes on worthy standards; he is not responsible for myopia. My colleague, Professor J. P. Frankel, has helped me with his candid opinions.

Professors Daniel Rosenthal and Allen Rosenstein have given constant encouragement and advice. A number of important changes have been made as a result of their suggestions.

I am especially grateful to Professor E. T. Jaynes of Washington University, St. Louis, who has given unselfishly of his time and energy to help me utilize his methods in this book. The approach to probability theory (Chapter 2) and the notation used to represent Jacobians (Chapters 9 and 13) are from some of his unpublished works.

My colleagues in the Department of Engineering at UCLA have been especially helpful. My graduate students have given support when they could ill afford the time. Mr. Robert Brenner read and criticized many early drafts. Mr. Simon de Soto not only experimented with different ways of teaching the material, he painstakingly proofread every line of the "next-to-last" manuscript. Mr. Robert Evans developed many of the proofs that were ultimately adopted.

Finally, I must acknowledge the support given by Dean L. M. K. Boelter who never doubted that the junior-year students could master this material. By his concept of the unified engineering curriculum and of an engineering department that is not fragmented into specialties, and by his encouragement, he made this audacious change in instruction possible. An academic atmosphere of this kind is difficult to find.

MYRON TRIBUS

ON THE USE OF THIS BOOK

This book has been planned so that it could be used at three levels of instruction: introductory, intermediate and advanced.

For an introductory treatment of two semesters (48 lecture hours per semester) the author has found the following time schedule satisfactory for third-year students: [1]

First Semester:

Chapter	1	5 hours
Chapter	2	12 hours
Chapter	3	4 hours
Chapter	4	5 hours
Chapter	5	3 hours
Chapter	6	8 hours
Chapter	8 –	6 hours
Chapter	9	5 hours

Second Semester:

Chapter 10	3 hours
Chapter 11	6 hours
Chapter 12	8 hours
Chapter 13	8 hours
Chapter 14	6 hours
Chapter 15	9 hours
Chapter 16	6 hours

It is not suggested that these allotted times will permit the students to "cover" each chapter thoroughly. Indeed, in an introduction one can merely develop the main idea of the chapter and then sample the available applications. The particular examples used may vary from one instructor to another. Each chapter has been written to do one of two things:

(1) Show how a microscopic premise provides a macroscopic consequence.
(2) Develop a methodology for problem-solving.

It has therefore not been difficult for an instructor to select the material suitable for his purpose.

[1] If students can be counted on to have adequate preparation in statistics, about 9 hours can be made available in the first semester and should be used to provide greater depth in the selected material. Alternatively, Chapter 7 or Chapters 10 and 11 might be introduced.

In our school, we do not separate students into electrical, chemical, civil, etc., curricula. In some schools, where this separation is still in vogue, the instructors have spent more time on applications especially suited to their specialities. Thus, in a one-semester course in engineering physics, if the students have already studied probability theory, the sequence might-well be:

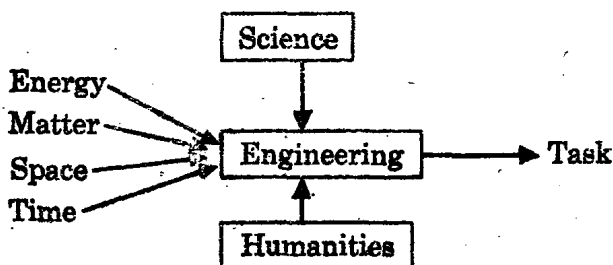|		
Chapter	2	3 hours
Chapter	3	3 hours
Chapter	4	3 hours
Chapter	5	3 hours
Chapter	6	7 hours
Chapter	7	7 hours (with Appendices)
Chapter	12	7 hours
Chapter	15	7 hours
Chapter	16	6 hours

Electrical engineers might wish to follow a similar sequence. Mechanical engineers might wish to emphasize Chapters 10 and 11 compared to Chapter 13 and Chapter 14 (and omit Chapter 7). Chemical engineers probably would prefer to emphasize Chapters 13 and 14.

For graduate study (or for seniors who already are familiar with the methods of macroscopic thermodynamics), the following schedule may be used:

Chapter	2	4 hours
Chapter	3	3 hours
Chapter	4	2 hours
Chapter	6	6 hours
Chapter	7	6 hours
Chapter	9	3 hours (Jacobians only)
Chapter	12	6 hours
Chapter	15	7 hours
Chapter	16	7 hours

INTRODUCTION

You are about to begin the study of one of the most fascinating and general subjects in science—energy and its relation to matter. When an engineer undertakes a task, he has as resources energy, matter, space and time. He uses these resources with the knowledge gained from science and from the humanities to perform a task which, we hope, is to the benefit of his fellow men. It

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                    ┌─────────┐
                    │ Science │
                    └─────────┘
                         │
                         ▼
 Energy                          
 Matter      ┌─────────────┐
             │ Engineering │ ──────► Task
 Space       └─────────────┘
 Time                    ▲
                         │
                  ┌────────────┐
                  │ Humanities │
                  └────────────┘
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is impossible to effect any physical change without utilizing, to some extent, the four ingredients: energy, matter, space and time. It is possible to do a task poorly by squandering resources, by building or designing systems which use too much fuel or are wasteful of materials or take up more space or time than is needed.

To know how to predict the behavior of a system, the engineer must have recourse to the knowledge of science. It is true that many engineers, through their own studies, contribute to science. (This book is the outcome of many such contributions.) Such contributions, however important they may be, do not form the mainstream of engineering activity.

Similarly, for help in judging what benefits man, the engineer must turn to the humanities. It is also true that engineering works have profoundly altered the values that sway our culture. These effects, too, are important, but they do not describe the mainstream of engineering activity.

The main activity of the engineer is the design or synthesis of improved systems to meet needs. To carry on this activity the engineer must understand how the four ingredients, energy, matter, space and time, are utilized.

This book is concerned with the first two of these quantities—energy and matter. We shall be considering these two subjects from the point of view of science and engineering. The scientific aspects will necessarily dominate our discussions. The engineering aspects will appear mainly in the examples and problems.

The Nature and Scope of Our Subject Stated broadly, "thermostatics" and "thermodynamics" encompass the study of the transformations of energy

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from one form to another.[1]   Since every physical event is accompanied by an energy transformation, it is clear that the study of thermodynamics embraces all of science and engineering.   Only through such study is it possible to see that separate fields such as mechanics, electromagnetics, chemistry and the properties of materials are not unrelated, but are linked together through the propositions and conclusions of thermodynamics.

A field of study as broad as thermodynamics must of necessity develop broad and powerful methods of attack upon problems.   These methods of thermodynamics will form the subject of our studies.   Examples will be introduced to illustrate the methods, but it is the methods not the examples that should be remembered.

The study of thermodynamics is an exercise in logic.   Exercises in logic generally fall into two parts.   The first part concerns definitions and is essentially a semantic effort.[2]   The second part is the actual logical manipulation. When difficulties with thermodynamics arise, students are best advised to spend time inquiring what they mean by the words they use.   That a careful choice and use of words is a difficult task cannot be denied.   On the other hand, the wisdom of thermodynamics is not available to those who would have knowledge without understanding or skill without effort.

Because the applications of thermodynamics occur in so many different fields, it would be foolish to try to study them all.   Instead, we shall take as examples those applications that illustrate the methods of analysis.   By taking this attitude, we depart from the currently popular "How to do it" books which, while valuable to the technician, do not prepare a man to tackle new problems. On the other hand, by concentrating upon the methods of analysis and keeping them constantly in view, it is our hope that analytical skills, fitting for a professional engineer, will develop.

Development of Macroscopic Thermodynamics   The concept of energy arises first in mechanics [3] where it is found that if one invents the function called "energy" certain very difficult problems can be easily solved.   Huygens (1629–95) and Newton (1642–1727), using the foundations of mechanics established by Galileo (1564–1642), both have been credited with recognizing that the *decrease* in gravitational energy ($mg\,h$), when a mass m descends a distance h under attraction per unit mass g, is equal to the increase in kinetic energy ($\frac{1}{2}\,mv^2$) at velocity v.   Newton concentrated his attention upon momentum, mv, while Huygens felt that the "vis-viva" (literally "force of liveliness") mv^2 (we now would say twice the kinetic energy) was the most important characteristic of the motion.   In 1661, Huygens demonstrated that

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[1] Thermostatics is concerned with equilibrium processes which do not depend upon time as an explicit variable. Thermodynamic problems involve time, i.e., dynamic considerations. We shall say "thermodynamics" when we mean both.

[2] "Semantics" is the study of the meanings attached to words.

[3] Bell, A. E., "The Concept of Energy," *Nature*, Vol. 151, p. 519, May 8, 1943.

he could calculate very easily the height to which pendulum bobs would rise upon impact by using the principle of the conservation of energy.

The difficulty which troubled our forebears prior to 1850 was that these energy methods of analysis seemed to work only in certain special cases. As long as the problem required consideration of forces of gravity, elastic springs or elastic collisions, the energy methods yielded correct answers. But when viscous forces, friction and inelastic collisions occurred, the method failed. It was the conversion of heat to work and work to heat that vexed these early scientists, and it is of historical interest to recall how this matter was resolved.

Genesis of First Law of Thermodynamics as an Empirical Observation The first law of thermodynamics (concerning convertibility of heat to work) is scarcely a century old. When the California Gold Rush was at its height, the first law had just reached a wide (but not general) acceptance. The second law (relating to the maximum efficiency of heat engines) was a bit older. In 1850, Clausius [4] began to refer to these laws as "principles" and to draw conclusions from them.

The first law could not be established until it was recognized that heat was a mode of energy transfer. But the understanding of heat required the development of the thermometer. Roller [5] gives Galileo credit for inventing the first precursor of the thermometer (1592). His "thermoscope" responded to changes in both pressure and temperature, and the scale was marked off "at pleasure." Sanctorius, a professor of medicine at Padua University and a colleague of Galileo, first used the thermoscope to detect fevers. In 1631, Jean Rey, a French physician, used the expansion of water to measure temperature. In 1641, the Grand Duke Ferdinand II of Tuscany developed a thermoscope which used the expansion of alcohol in a sealed tube. He also used a novel type of thermoscope in which different-sized glass bubbles were inserted in alcohol. As the density changed, various bubbles would sink or rise. Roller gives a most interesting account of the slow evolution of the scales attached to thermometers (i.e., starting with two marks: "the greatest summer heat" and "the severest winter cold"). In 1759, Joseph Black was Professor of Chemistry at Glasgow University. Roller credits Black with first drawing the distinction between "temperature" as a *measure of hotness* and "heat" as a measure of the *quantity* of heat. Black was first to define "heat capacity," deducing the need for this concept from a study of the mixing experiments of G. D. Fahrenheit (1668–1736). The "method of mixtures" (e.g., mixing hot mercury and cold water and measuring the temperatures before and after mixing) is still used today to determine heat capacities. This

[4] Clausius, R., "Ueber die bewegende Krafte der Wärme und die Gesetze, welche sich daraus fur die Wärmelehre selbst ableiten lassen." *Pogg. Ann.*, Vol. 78, pp. 368–500 (1850).

[5] Roller, D., *The Early Development of the Concepts of Temperature and Heat—the Rise and Decline of the Caloric Theory*, Harvard University Press, 1950.

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method was first clearly understood by Black. Black also first clearly recognized the heat release that occurs on freezing (latent heat) and the heat absorbed upon boiling (heat of vaporization). One of Black's pupils was James Watt, who applied Black's ideas to the improvement of the steam engine.

The establishment of methods of measurement that could reveal the laws of heat transfer soon focused attention on the question "What is heat?"

The Caloric Theory   Although Francis Bacon (1620) thought that heat was a "form of motion," he had no strong evidence to prove this assertion. Newton thought heat was a vibration of a "rare and subtile fluid" which pervaded all space.[6] But the experiments of Black and others made it seem impossible that heat was "motion." In 1779, Cleghorn set forth the "caloric theory" that [5]:

(1) Heat is an elastic fluid.
(2) Heat is attracted differently by different matter.
(3) Heat is indestructible and uncreatable.
(4) Heat can be sensible or latent.
(5) Heat has no appreciable weight.

Lavoisier, in 1787, called the fluid "caloric." This theory of heat held the most popular support for many years, even after it was demonstrated to be false. It is still believed by some students! The casting off of the false ideas generated by the caloric theory will be one of our tasks.

The question concerning the existence of "caloric" seemed to hinge upon its weightlessness. Robert Boyle showed in 1665 [5] that water frozen or unfrozen weighed "not one grain difference." In 1785, however, George Fordyce, a British physician, reported an *increase* in the weight of frozen water of one part in 129,000.

Benjamin Thompson (1753–1814), an American whose sympathies and spying for the British side during the American Revolution made it healthier for him to live abroad, was the first to provide data leading to the overthrow of the caloric theory. Thompson, who had become Count Rumford, began a series of experiments lasting 12 years (1787–1799) to check Fordyce's results. Using techniques that would reveal differences in weight to one part in one million, Rumford concluded, after many difficult experiments, that the caloric fluid, if it existed, must indeed be weightless. We now know, of course, that the addition of energy, in any form, to a body increases its mass by an amount $m = E/c^2$ where c = velocity of light. In all reactions except nuclear ones, this change in mass is far too small to measure. [For example, since $c = 186,000$ miles/sec, we compute that 1 Btu (= 778 ft-lb) added to 1 lb of water increases the mass by only one part in 4×10^{13}. Rumford would have needed a balance almost a million times more sensitive than he had to detect this

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[6] Chalmers, T. W., *Historic Researches*, Morgan Brothers, London, 1949.

change.] The failure to find a weight for "caloric" convinced Rumford that heat could not be a fluid.[7]

Rumford's second attack on the caloric theory proved its eventual undoing. In a series of elaborate and careful experiments on a gun-boring machine in Bavaria, he proved that the heat released by the drill was directly proportional to the work expended by the horses that pulled the drill bar round and round. In his report, published in 1798, he was careful to point out that his experiments were made on the superfluous part of the casting which is ordinarily cut off the cannon anyway, so that no harm had been done by his "philosophical researches." [5]

Now, it is common, particularly in nonscientific circles, to portray men of science as stiff, unemotional creatures, who upon entering a monastic life of science put aside all passions and govern their thoughts only by observation and logic. A falser picture would be difficult to paint. The thrill of science is not only in *knowing* but also in *telling* others. So when a new idea appears, which, if true, would make it necessary for some scientists to retract their previous views, it is only natural that the new idea will be received with something less than enthusiasm.

In his study of the history of the first law, Epstein [8] has shown how the physicists of the day did not wish to think about the results of Davy and Thompson, but held strongly to their "caloric." It was the men of medicine, rather than the physicists, who took up the matter. They were attempting to account for the heat released by the human body and, due to faulty data on the combustion of hydrogen, they found they could not completely account for the body's energy by measuring, in the laboratory, the heat liberated from the combustion of food. The explanation they proposed was that the extra energy came from friction in the blood vessels. This view seemed rational to the doctors, in view of the data from Thompson's gun-boring equipment. Later experiments produced revisions in the data for the heat of combustion of hydrogen, making it clear that the frictional contribution by the blood vessels did not have to be invoked and that the energy released by the food could be accounted for by simple heats of oxidation. Thus, to the doctors must go the credit for first accepting the modern theory and abandoning the "caloric."

When Dr. Julius Robert Mayer attempted to bring this view to the attention of the physicists of the day, he met that special opposition reserved for purveyors of new ideas. Mayer was a ship's doctor aboard a schooner in the East Indies, in 1840, when he persuaded himself of the general validity of the first law. Some of the reasoning he used we would now consider illogical, and the evidence was insufficient, but these facts alone cannot account for the treatment

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[7] The reader is left to speculate whether an impartial committee asked to evaluate Rumford's work would have supported the deduction that, because he measured no weight change, the fluid did not exist.

[8] Epstein, P. S., *Textbook of Thermodynamics*, Wiley, New York, 1937, p. 30.

accorded him. His first manuscript on this subject was sent to the leading scientific journal in Germany and was neither acknowledged nor published.[9] His subsequent publications (1842) were publicly ridiculed. Meanwhile, James Prescott Joule, who, quite independently, was convinced of the new view also, performed a series of experiments designed to test the "mechanical theory of heat." He converted work to heat via such means as letting falling weights churn a measured amount of water with paddle wheels, by passing electrical currents through resistors and by measuring the work input to an air compressor. Mayer had calculated the mechanical equivalent of heat before Joule by analyzing the heat required to warm gases at constant pressure and at constant volume, but because his work was based upon inaccurate data for the heat capacities of air, he did not obtain an accurate value for the ratio between heat and mechanical units (i.e., Btu per ft-lb). Joule's more correct and direct data appeared just at the time of the death of Mayer's children and, in the ensuing struggle to establish priority of discovery, Mayer fared very poorly. In discouragement, he attempted suicide, breaking both legs in a leap from a third story. He was declared insane, and for awhile, legally dead, but finally in 1869 he was able again to take part in public meetings and obtain some measure of honor and recognition.[5]

Despite the example of Robert Mayer (and so many others), people today still persist in picturing men of science as queer passionless robots. It is rather our detached way of talking about the history of science that has distilled their passion from them.

Today it is easy for us to say that heat and work are manifestations of energy, that energy can neither be created nor destroyed. The men who stubbornly refused to accept this proposition are now buried, and, if not forgotten, at least are remembered for other reasons. Since their passing, new generations of students have been confronted with the need to profess a belief in the first law or they cannot pass their courses! But we should not forget that the principle of the conservation of energy was once a center of controversy and the "caloric" theory died stubbornly.

History of Second Law as an Empirical Observation   It had been known that heat flows from a higher to a lower temperature, but never in the reverse direction without the aid of an agent external to the system. In 1824, Sadi Carnot,[10] a French military engineer, considered this phenomenon and was able to deduce from it that heat could not be converted to work without the existence of a temperature difference. Carnot's contribution was expanded upon by Kelvin and later by Clausius, who in 1850 made it one of the two principles upon which he based his "mechanical theory of heat" (1850). Except for an attempt by Caratheodoray, which is accepted by some thermo-

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[9] Roller, D., *opus cit.*

[10] Carnot's work has been translated into English and is published by the American Society of Mechanical Engineers under the title "Reflections on the Motive Power of Heat" (1943).

dynamicists and rejected by others, the demonstration of the second law as given by Carnot and Clausius has been unchanged, in essence, in over 100 years.

Development of Statistical Methods   The discoveries mentioned above were concerned with what has been called the "phenomenological" or "macroscopic" [11] approach to thermodynamics. No particular concept concerning the fundamental particles of matter needed to be invoked as a basis for Clausius' theory. However, parallel to these developments in thermodynamics there were developments going on in kinetic theory and atomic physics.

One of the premises of physics is that, through an understanding of the behavior of the smallest particles and their interaction, one should be able by logical steps to explain and predict the behavior of complicated systems composed of many particles.

The earliest known attempts at an atomistic theory were made by Democritus (born in 485 B.C.), who suggested that the properties of matter were determined by the properties of the "atoms" of which they were composed. The reader of this book is presumed to be familiar with the growth of this view in chemistry and physics. We need not recount the various achievements that led to the adoption of the concept of valence, of bonds, of crystal structure, of the kinetic theory and of the experiments demonstrating the existence of various particles. Our interest lies in the development of methods whereby the characteristics of the parts can be used to determine the character of the whole.

These methods must be statistical in nature, for the same reason that statistical methods are employed in other fields. (The reasons will be elaborated upon in Chap. 2.) Various scientists, among them Daniel Bernoulli, James Clerk Maxwell and Ludwig Boltzmann, showed, in special cases, how to use statistical methods to compute the properties of gases. In 1901, Josiah Willard Gibbs, a professor at Yale University, published a book titled *Elementary Principles in Statistical Mechanics*. In this book, Gibbs showed how the properties of the individual particles could be combined, by suitable averaging techniques, to predict those properties accessible to beings whose senses are as gross as our own. Gibbs' work preceded the quantum theory and, therefore, while his methods were correct, they did not, in some instances, give rise to the correct (i.e., verifiable) answers. Gibbs, himself, only referred to his results as representing an "analogy," and it may be speculated that he grappled with the resolution of the problem up to his death in 1903. The discovery of the quantum theory by Max Planck provided the missing clue. Quantum theory is a physical theory—it tells us things about physical systems. Statistical mechanics is a mathematical theory—it tells us how properties are to be combined statistically. Quantum theory provides the "input information" so that the methods of Gibbs

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[11] The *macroscopic* view consists of looking at gross or average properties, such as density, color, volume or temperature. The *microscopic* view considers valences, bonds, atomic properties, etc.

may be employed. The inadequacies of Gibbs' results lay not with his methods but with the information he was forced to feed into his methods. A number of excellent books, especially the ones by Tolman, by Landau and Lifschitz, and by Fowler and Guggenheim, have shown how one may explain all of the results of the classical macroscopic thermodynamics by the use of quantum theory and Gibbs' methods.

But despite these successes there has been something lacking. In the first place, although Gibbs used the word "elementary" in the title of his book, the methods have not been considered "elementary" by any other person. Quite formidable mathematical problems must first be resolved before one can apply Gibbs' methods as he did. What has been needed is a simple way of accomplishing, without loss of rigor or generality, what could only be accomplished with great effort using Gibbs' approach.

In 1948, Claude Shannon of the Bell Telephone Laboratories published a paper dealing with communication theory. His concern was with the means whereby an individual conveys information through a channel to another individual. Leon Brillouin, in 1953, recognized that Shannon's concepts could be applied to the problem of the experimenter in the laboratory who receives messages from his instruments.

In 1957, E. T. Jaynes of Stanford University published a paper in which he showed, starting with Shannon's results, how one could obtain in an elementary way all of the results given by Gibbs. It is difficult to overestimate the value to scientific education of this contribution. At one fell swoop the enormous conceptual difficulties inherent in Gibbs' approach have been swept away. It now becomes possible to begin by considering the properties of the smallest particles and by simple mathematical methods to deduce the properties of large systems. The results obtained by Joule, Mayer, Carnot, Maxwell, Boltzmann and Gibbs are seen in a new light. It is no longer necessary to cover the development of thermodynamics in the same way as the subject developed in history. New generations of students can, in shorter time, reach a state of understanding heretofore impossible for more than a small number of persons. It is this purpose that prompted the writing of this book.