



# THE GENERAL THEORY OF THERMODYNAMICS

AN INTRODUCTION TO THE STUDY OF  
THERMODYNAMICS

BY

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## PREFACE

This little book is intended to serve as an introduction to the study of thermodynamics, and is planned for the use of students who have some acquaintance with the calculus of functions of more than one variable. Its distinctive purpose is to develop the general laws of thermodynamics with logical consecutiveness and mathematical clarity, and thus to establish these laws in a manner that can be thoroughly understood.

In the pursuit of cogency much care has been taken to leave no gaps in the chain of reasoning by which the results of the theory are obtained. For the same reason, various familiar expedients have been avoided. Thus no inexact differential expression is represented by the notation for a differential; no conclusions are based on the properties of non-existent "ideal gases"; and it is not assumed that the general reversible cyclic change of state of the general body must be the limiting effect of the operation of a set of Carnot cycles.

The text deals exclusively with general principles; no applications are considered. The treatment begins with the first law of thermodynamics, continues with the second law, the theorem of Carnot, the scale of absolute temperatures, and the entropy law, and is concluded by a critical study of the dissipation law and of an important deduction from it. Study of the text is facilitated by synopses of successive stages of the reasoning, and by a final review of the whole argument. A conscious effort has been made to distinguish sharply between theorems based on physical grounds and logical consequences deduced from such theorems. To ensure the correctness and completeness of the logical work, the physical theorems are formulated as mathematical statements, which are then developed by purely analytical means.

Some characteristic features of the book are as follows:

1. Attention is early directed to the existence of distinct regions of the states of thermodynamic equilibrium of a given

body. This increases the intelligibility of the subsequent exposition, and closes the door against the use of such misleading phrases as "the variables that determine the states (of thermodynamic equilibrium) of the body."

2. The difficult idea of reversibility is carefully explained.

3. The idea of a Carnot cycle is introduced with an unusual breadth of view. Thus cycles of different types are presented both in a diagram in space and in the projections of this diagram on the coordinate planes; a compression-expansion cycle having an isotherm at constant volume is shown; and the possibility of cycles in an isothermal region, and indeed of cycles of even more unexpected types, is indicated. Finally, to facilitate the applications of the second law, the useful concept of a chain or "sequence" of Carnot cycles is introduced, and attention is directed to no fewer than five distinct types of sequence which operate between equal end-temperatures.

4. It is proved that the quantity of work absorbed in the operation of a sequence has the sign of the quantity of heat absorbed on the lower terminal isotherm, and that these quantities vanish together. The theory fails in completeness of logical form if this essential preliminary theorem is merely more or less unconsciously assumed.

5. On the understanding that work  $W$  is absorbed by any sequence operating between temperatures  $t_1$  and  $t_2$  and absorbing heat  $x$  at  $t_1$ , it is established, for all values of  $x$  and all relative values of  $t_1, t_2$ , that  $W$  is a single-valued continuous function  $W(x, t_1, t_2)$  of the independent  $x, t_1, t_2$ , and that  $W(x, t_1, t_1) = 0$ .

6. The form of dependence of  $W(x, t_1, t_2)$  on  $x$  is determined by solution of a certain functional equation; whereupon the theorem of Carnot is obtained.

7. Then the form of dependence of  $W(x, t_1, t_2)$  on  $t_1, t_2$  is determined by solution of another functional equation; whereupon it becomes clear that the absolute temperature is defined by a positive, increasing, single-valued, continuous function  $\theta(t)$ .

8. On the understanding that the heat-element for a selected auxiliary gas is a linear differential form  $DQ$ , it is shown, with the aid of Green's theorem, that the line integral of the expres-

sion  $DQ/\theta$ , taken along any reversible cyclic change of state of the gas, is equal to zero. And it is made manifest that the reasoning employed provides a differential equation for the absolute temperature.

9. By coupling the general reversible cyclic change of state of the general body with a cyclic change of state of the auxiliary gas, it is then proved that the absolute temperature is an integrating divisor of any regional heat-element, which establishes the existence of the entropy of the body for the region. Stress is laid upon the fact that this result cannot be deduced unless it is known that the regional heat-element is a linear differential form.

10. In the deduction of the criterion of stability of the equilibrium of a body subject to no force other than a uniform and normally directed pressure,

$$\delta E + p\delta V - \theta\delta S \cong 0,$$

it is made clear that the quantities  $\delta V, \delta S, \delta E$  are *finite differences*, and that the quantities  $p, \theta$  are *constants*, — which denote the pressure and the absolute temperature of the body in the given state of equilibrium.

It is hoped that the book may be found useful as a classroom text in the teaching of thermodynamics to students of physics and of physical chemistry. Conceivably also it may attract the attention of mathematicians who would welcome an exposition which can be read in an evening or two. For it attempts to present in clear and correct form the minimum amount of thermodynamics that every mathematician should know. The book should also be of service to ambitious students of the thermodynamics of engineering, and to practicing heat-power engineers who wish to improve their understanding of the theory of their subject.

Acknowledgment is due to my son, Bertram, for the preparation of the drawings.

J. E. TREVOR

# CONTENTS

| CHAPTER   | PAGE |
|---|------|
| I. THERMODYNAMIC STATES OF BODIES. . . . .  | 1    |
| Body, 1 · Temperature, 1 · Quantity of Heat, 2 · Thermodynamic State, 2 · Change of Thermodynamic State, 3 · Supplementary Changes of State, 3 · State of Thermodynamic Equilibrium, 3 · Regions of States of Thermodynamic Equilibrium, 4 · Synopsis, 7  |      |
| II. THE ENERGY OF A BODY. . . . .   | 8    |
| Equivalence of Work and Heat, 8 · Heat-Units, 8 · The First Law of Thermodynamics, 9 · The Energy Law, 10 · Different Paths, 11 · Conservation of Energy, 13 · A Warning, 13 · Synopsis, 14   |      |
| III. SEQUENCES . . . . .  | 15   |
| Compression and Expansion, 15 · Reversible Paths, 16 · Paths not Reversible, 19 · Carnot Cycles, 20 · Varieties of Carnot Cycles, 25 · The Case $t_2 = t_1$ , 26 · Sequences, 27 · Synopsis, 30   |      |
| IV. THE SECOND LAW OF THERMODYNAMICS . . . . .  | 32   |
| V. A THEOREM ON SEQUENCES . . . . .   | 34   |
| VI. THE WORK ABSORBED BY A SEQUENCE . . . . .   | 38   |
| $W$ is Independent of the Working Bodies, 38 · The Function $W$ , 41 · Synopsis of Chapters IV, V, VI, 42   |      |
| VII. THE FORM OF THE FUNCTION $W$ IN $x$ . . . . .  | 43   |
| Dependence of $W$ upon $x$ , 43 · Synopsis, 44  |      |
| VIII. THE FORM OF THE FUNCTION $W$ IN $t_1, t_2$ . . . . .  | 45   |
| Dependence of $W$ upon $t_1, t_2$ , 45 · Formulating the Increment of $W$ , 45 · Theorems and Equations for Reference, 46 · A Functional Equation for $q(t_1, t_2)$ , 46 · The Reciprocal of $q(t_1, t_2)$ , 46 · The Sign of $q(t_1, t_2)$ , 47 · The Form of $q(t_1, t_2)$ , 47 · The Form of the Function $W(t_1, t_2)$ , 48 |      |
| IX. THE ABSOLUTE TEMPERATURE . . . . .  | 49   |
| The Ratio $Q/x$ , 49 · Definition of the Absolute Temperature, 49 · Synopsis of Chapters VIII and IX, 50  |      |

# X      GENERAL THEORY OF THERMODYNAMICS

| CHAPTER   | PAGE |
|---|------|
| X. THE GENERAL CYCLIC CHANGE OF STATE OF AN<br>AUXILIARY FLUID . . . . .  | 52   |
| A Theorem on Carnot Cycles, 52 · An Auxiliary Fluid, 52 ·<br>Formulation of the Theorem on Carnot Cycles, 53 · The General<br>Cyclic Change of State of the Fluid, 54 · The Case of $n$ Vari-<br>ables, 55 · The Absolute Temperature, 55 · Synopsis, 57  |      |
| XI. THE ENTROPY OF A BODY . . . . .   | 59   |
| The General Cyclic Change of State, 59 · Heat-Elements, 60 ·<br>The Entropy of a Body, 61 · The Formulation of Heat-<br>Elements, 62 · Integrating Factors of Heat-Elements, 64 ·<br>Synopsis, 68   |      |
| XII. THE SCALE OF ABSOLUTE TEMPERATURES . . . . .   | 70   |
| A Differential Equation for $\theta$ , 70 · The Porous Plug Effect,<br>71 · A New Differential Equation for $\theta$ , 72 · Exercise, 73 ·<br>Synopsis, 73  |      |
| XIII. DISSIPATION . . . . .   | 75   |
| Paths of Least Resistance, 75 · Processes of Diverse Types, 76 ·<br>Uncontrollable Processes, 82 · The Postulate of Dissipation, 84 ·<br>Thermally Isolated Bodies, 85 · Synopsis, 87   |      |
| XIV. A CRITERION OF STABILITY . . . . .   | 89   |
| An Application of the Dissipation Law, 89 · A Criterion of<br>Stability, 90 · Synopsis, 92  |      |
| XV. REVIEW . . . . .  | 94   |
| Definitions, 94 · Energy, 94 · Reversibility, 94 · The Second<br>Law, 95 · The Function $W$ , 95 · Dependence of $W$ on $x$ , 95 ·<br>Dependence of $W$ on $t_1, t_2$ , 96 · Absolute Temperature, 97 · A<br>Theorem on Carnot Cycles, 98 · Entropy, 98 · Scale of Abso-<br>lute Temperatures, 100 · Dissipation, 100 · An Analogy, 100 |      |
| INDEX . . . . .   | 103  |

# THE GENERAL THEORY OF THERMODYNAMICS

## CHAPTER I

### THERMODYNAMIC STATES OF BODIES

**Body.** In this book the term *body* will be employed to designate a definite material object. If the object is to remain a body, no part of it may be removed and no material may be added to it while it is under consideration. A quantity of liquid water *together with* a quantity of overlying steam is a body; but the liquid portion of this object is not a body when a rise of the temperature of the object converts a part of the liquid into steam. If a body *B* consists of separate masses of ice and common salt, it remains the body *B* when the ice is melted, when the salt is dissolved in the liquid thus formed, and when the resulting solution is partly decomposed by electrolysis. The physical and chemical condition of an object may be altered in any way without the object's ceasing to be a body.

**Temperature.** A thermometer is an instrument whose numerical scale readings increase with the hotness of the instrument, and may be considered to be in continuous one-to-one correspondence with the degree of this hotness. It may be an ordinary mercury-in-glass thermometer, a platinum-resistance thermometer, a gas thermometer filled with hydrogen or with some other gas, or a mere column of kerosene in a slender glass tube of uneven bore. For the present we shall make no selection. We shall consider the scale readings of any particular instrument to be values of the *temperature*  $t$  of that particular *arbitrary* scale.

The temperature of a body may be *uniform* or not, and if uniform it may be *constant* or not. When uniform and constant it



may be measured by establishing temperature equilibrium between the body and a thermometer, since it is observed that contiguous bodies having different temperatures come spontaneously to a common temperature. The uniform temperature  $t$  of a body is a real variable.\*

The standard temperature scales are those of the constant volume gas thermometer filled with an arbitrary mass of hydrogen supporting the pressure  $p_1$  of 100 cm of mercury at the freezing temperature of water. On the centigrade and Fahrenheit scales the freezing temperature  $t_1$  and the boiling temperature  $t_2$  of water under the pressure 1 atm are set at

$$\begin{array}{ll} t_1 = 0^\circ \text{C}, & t_2 = 100^\circ \text{C}; \\ t_1 = 32^\circ \text{F}, & t_2 = 212^\circ \text{F}. \end{array}$$

When the temperature of the hydrogen is raised, its pressure becoming  $p_2$  at  $t_2$ , the temperature increases one centigrade degree of the hydrogen scale with each increment  $(p_2 - p_1)/100$  of the pressure, and it increases one Fahrenheit degree with each increment  $(p_2 - p_1)/180$  of the pressure.

**Quantity of Heat.** When a hot block of copper is in contact with a cold block of iron, when a hot bullet is dropped into ice, and when a kettle of water boils on a hot stove, "heat" is said to pass from the copper to the iron, from the bullet to the ice, and from the stove to the boiling water. In general, *quantities of heat* are defined with reference to measurement by means of a calorimeter, and the unit in which the measurement is expressed is the quantity of heat requisite to raise the temperature of unit mass of water one degree on a specified temperature scale, under a specified constant pressure.

**Thermodynamic State.** The thermal and mechanical properties of a given body of gas can be altered by heating or cooling the body, and by compressing or expanding it. In general, the thermal and mechanical properties of any body can be altered by positively or negatively adding *heat* and *work* to it. When this is done we shall say that the *thermodynamic state* of the body has been altered.

\* For an interesting and thoughtful historical and critical discussion of thermometry, see Mach, *Wärmelehre*, pp. 3-77. Leipzig, 1896.

**Change of Thermodynamic State.** By a *change of thermodynamic state* of a body shall be meant a transformation of one thermodynamic state into another. It is determined solely by the end states. The *path* of a change of state is the set of intermediate states. A given change of state can occur on different paths; as when a body of gas is slowly expanded from an initial volume  $V_1$  to a final volume  $V_2$  at constant temperature; or is expanded from  $V_1$  to  $V_2$  when thermally insulated, and its consequent fall of temperature is overcome by adding heat at the constant volume  $V_2$ ; or is allowed to expand abruptly into an exhausted space having the volume  $V_2 - V_1$ , any consequent change of temperature being corrected by subsequent addition or abstraction of heat.

**Supplementary Changes of State.** If a heavy piston confines a body of air in a vertical cylinder, and the released piston falls to a lower position with a consequent decrease of volume and increase of temperature of the air, the changes of state of the piston and of the air shall be said to *supplement* each other. If two blocks of metal having initially different temperatures are brought into contact, whereby both come to a common temperature, the change of state of each block *supplements* that of the other. In general, supplementary changes of state are the concurrent changes of state of two bodies, which together constitute the set of all the bodies participating in the process.

**State of Thermodynamic Equilibrium.** When a body has a constant uniform temperature and all its parts are at rest, it shall be said to be in a state of *thermodynamic equilibrium*. For it is then in thermal and in dynamic equilibrium with the contiguous bodies. The state of thermodynamic equilibrium of a body of gas can be specified by numerical values of its temperature and of the pressure that it supports. The state of a body of liquid water and overlying steam in a closed boiler can be specified by the values of the temperature of the body and of the volume that it occupies. In any case it is always possible similarly to describe the state of thermodynamic equilibrium of a given body by a set of numerical specifications that are sufficient for the purpose to be served. In some cases the quantities

specified may be the imposed forces and the imposed temperature. In other cases they may not. The state of a body of coexistent water and steam, for example, cannot be specified by values of the pressure and the temperature of the body.

**Regions of States of Thermodynamic Equilibrium.** It is very important to realize that the states of thermodynamic equilibrium of a given body lie usually, if not always, in contiguous regions of state that are wholly distinct from one another. This circumstance is illustrated by Fig. 1, in which the pressure  $p$  atm of carbon dioxide is plotted against the specific volume  $v$  cm<sup>3</sup> (the volume of one gram) and the temperature  $t$  deg C of a body of the substance. The figure is a graph of the surface

$$p = f(v, t),$$

for a restricted range of each of the variables.

The surface is crossed from left to right by a number of isothermal lines in which planes perpendicular to the axis of  $t$  cut the surface. An isotherm for a temperature near 0 deg C falls steeply through the liquid field as the volume increases in isothermal expansion of the liquid; then horizontally traverses the evaporation field as evaporation proceeds at constant temperature and pressure; and finally falls gently through the vapor field in isothermal expansion of the resulting vapor. The evaporation field thus forms a cylindrical surface, perpendicular to the  $t, p$  plane and terminating at the "critical point," where it touches the isotherm  $t = 31.35$  deg C = 88.4 deg F. The highest isotherm in the figure traverses the field for homogeneous fluid, without a break.

From any point in the liquid field, a fall of temperature at constant pressure carries the representative point to the edge of a steep narrow cylindrical surface representing the fusion field, which the representative point traverses in the conversion of liquid into solid. Further cooling carries the point into the steep surface representing solid states at low temperatures.

Under the high pressure  $p = 2800$  kg/cm<sup>2</sup> = 271 atm = 4000 lb/in<sup>2</sup>, as is represented in the smaller figure, the cylindrical fusion field meets two similar cylinders. In the first of these the ordinary

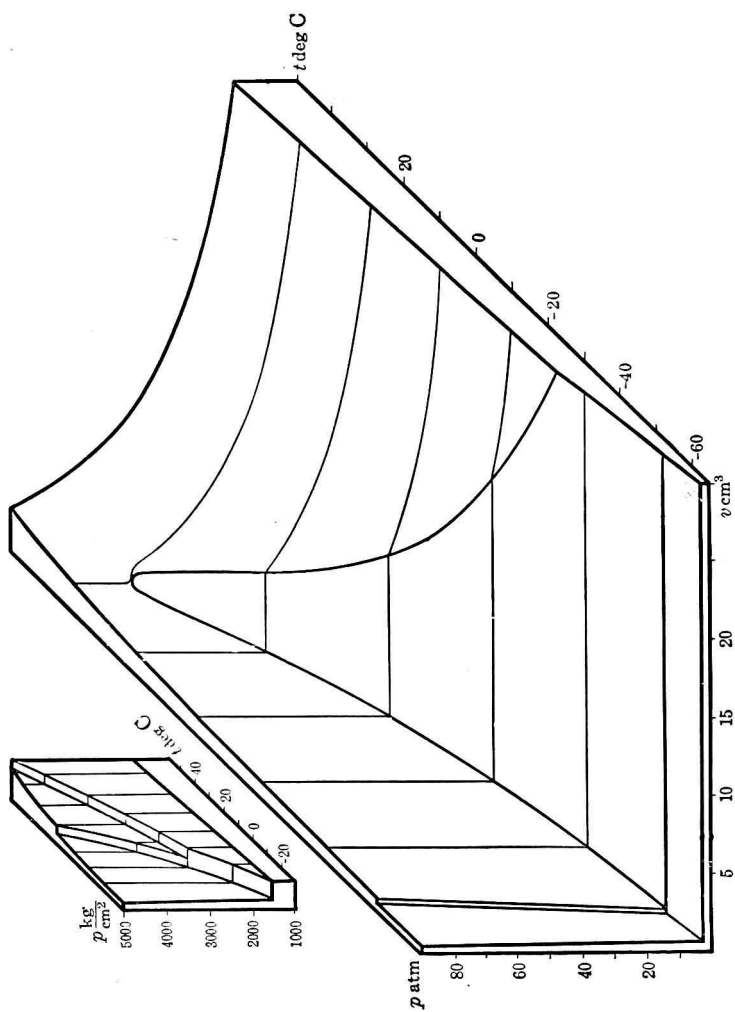


FIG. 1

solid is converted into a less dense solid form, and in the second this form is converted into liquid. So the last cylinder is a fusion field separating the field of the less dense solid states from the field for liquid.

It is thus clear that the fields for homogeneous fluid, for the ordinary solid, and for the less dense solid, as also the evaporation field, the field for transformation of the two solids, and the two fusion fields, form contiguous regions of state that are wholly distinct from one another. The function

$$p = f(v, t),$$

whose graph we are considering, has different *forms* in the different regions.

Then, too, it should be noted that the states of certain regions are not determined by the variables  $v, t$  at all. Other variables must be chosen. For example, in Fig. 1 consider the horizontal isotherm that is drawn through the point where the fusion field meets the evaporation field. A point on this line represents a state of coexistent liquid, vapor, and solid masses. By slow heating or cooling, the distribution of the total mass between these "phases" is continuously altered at constant  $v, t$ , and  $p$ . Hence a single point represents a continuous set of states; the variables  $v, t$  do not determine the states. At times it may even be desirable to employ different sets of independent variables for different regions. If  $p, t$  are chosen independent in a field of vapor states, another choice must be made for the contiguous evaporation field. For these variables do not determine states of coexistent masses of liquid and vapor.

The foregoing illustration is a simple one. More extensive possibilities are afforded by mixtures. When the state of an unsaturated solution of common salt in water is varied by compression or expansion and heating or cooling, we can obtain states of coexistent solution and vapor, or solution and ice, or solid salt and vapor, or salt and ice; we can obtain states of coexistent masses of any three of the phases: solution, salt, vapor, and ice; and we can obtain states in which all four phases coexist. The possibilities are increased when water is mixed with a salt which combines with it to form solid hydrates

of definite compositions. In general, the realizable states of thermodynamic equilibrium of a given body form distinct regions of state. And it must be remembered that the states of different regions are not always determined by the same independent variables.

**Synopsis.** A *body* is a definite material object. The uniform *temperature*  $t$  of a thermometer, expressed with reference to an arbitrary scale, is a real variable. A *quantity of heat* is a measurable quantity. Changes of physical state effected by adding positive or negative quantities of heat and work to a body are changes of *thermodynamic state*. A *change of state* is the transformation of one state into another; it is determined by the end states. The *path* of a change of state is the set of intermediate states. When an entire thermodynamic process consists of changes of state of two bodies, these changes of state *supplement* each other. When a body has a constant uniform temperature, and is at rest, it is in a state of *thermodynamic equilibrium*. The states of thermodynamic equilibrium of bodies form in general distinct continuous *regions* of states.

## CHAPTER II

### THE ENERGY OF A BODY

**Equivalence of Work and Heat.** It is a familiar fact that expenditure of work against friction produces heat. And it is a well-known experimental fact that *any mechanical operation expending a quantity of work against friction supplements an absorption of a quantity of heat proportional to the work expended.*

It follows that every absorption or development of heat by a body has a mechanical aspect, in that an absorption can be imagined supplemented by a mechanical operation, and a development can be imagined replaced by one. Hence quantities of work and of heat can be expressed in the same unit. If a development of 5 foot-pounds of work supplements an absorption of 1.62 calories of heat, we may say that 5 foot-pounds of work is developed and 5 foot-pounds of heat is absorbed; or we may say that 1.62 calories of work is developed while the equal quantity of heat is absorbed. *Henceforth, whenever quantities of work and of heat are considered together, it shall be understood that they are expressed in the same unit.*

**Heat-Units.** Various heat-units are in use. The *standard calorie* is the quantity of heat requisite to raise the temperature of one gram of water from  $15^{\circ}$  to  $16^{\circ}$  on the centigrade scale of the standard hydrogen thermometer, under the pressure of one atmosphere. The *mean calorie* is  $\frac{1}{1.00}$  of the quantity of heat absorbed when the temperature change is from the freezing to the boiling temperature, under the same pressure. The *British thermal unit*, the "*B.t.u.*," is the quantity of heat absorbed by one pound of water when its temperature rises one degree from  $t = 60^{\circ}$  on the Fahrenheit scale of the hydrogen thermometer under atmospheric pressure. Note that  $60^{\circ} \text{ F} = 15.5^{\circ} \text{ C}$ . The *mean B.t.u.* is  $\frac{1}{1.80}$  of the quantity of heat absorbed when the

temperature change is from the freezing to the boiling temperature. The "mean" units are more accurately known than the others described, because of the disturbing effect of the steepness with which the specific heat of water changes near 60° F. A conversion table, with entries to three significant figures, is inserted here to direct attention to the relative values of various units. The letter *t* in the table stands for *ten*. Thus

$$2.33 \text{ } t^{-3} = 2.33 \times 10^{-3} = 0.00233.$$

CONVERSION TABLE

| g-cm                        | ft-pdl                      | Joule<br>=10 <sup>7</sup> erg | ft-lb                       | Mean<br>cal                 | lit-atm                     | Mean<br>B.t.u.              | ft <sup>3</sup> -atm        | Watt-hr                     | H.p.-hr                      |
|-----------------------------|-----------------------------|-------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|------------------------------|
| 1.00                        | 2.33 <i>t</i> <sup>-3</sup> | 9.81 <i>t</i> <sup>-5</sup>   | 7.23 <i>t</i> <sup>-5</sup> | 2.34 <i>t</i> <sup>-5</sup> | 9.68 <i>t</i> <sup>-7</sup> | 9.30 <i>t</i> <sup>-8</sup> | 3.42 <i>t</i> <sup>-8</sup> | 2.72 <i>t</i> <sup>-8</sup> | 3.65 <i>t</i> <sup>-11</sup> |
| 4.30 <i>t</i> <sup>2</sup>  | 1.00                        | 4.21 <i>t</i> <sup>-2</sup>   | 3.11 <i>t</i> <sup>-2</sup> | 1.01 <i>t</i> <sup>-2</sup> | 4.16 <i>t</i> <sup>-4</sup> | 4.00 <i>t</i> <sup>-5</sup> | 1.47 <i>t</i> <sup>-5</sup> | 1.17 <i>t</i> <sup>-5</sup> | 1.57 <i>t</i> <sup>-8</sup>  |
| 1.02 <i>t</i> <sup>4</sup>  | 2.37 <i>t</i>               | 1.00                          | 7.38 <i>t</i> <sup>-1</sup> | 2.39 <i>t</i> <sup>-1</sup> | 9.87 <i>t</i> <sup>-3</sup> | 9.49 <i>t</i> <sup>-4</sup> | 3.49 <i>t</i> <sup>-4</sup> | 2.78 <i>t</i> <sup>-4</sup> | 3.73 <i>t</i> <sup>-7</sup>  |
| 1.38 <i>t</i> <sup>4</sup>  | 3.22 <i>t</i>               | 1.36                          | 1.00                        | 3.24 <i>t</i> <sup>-1</sup> | 1.34 <i>t</i> <sup>-2</sup> | 1.29 <i>t</i> <sup>-3</sup> | 4.73 <i>t</i> <sup>-4</sup> | 3.77 <i>t</i> <sup>-4</sup> | 5.05 <i>t</i> <sup>-7</sup>  |
| 4.27 <i>t</i> <sup>4</sup>  | 9.93 <i>t</i>               | 4.18                          | 3.09                        | 1.00                        | 4.13 <i>t</i> <sup>-2</sup> | 3.97 <i>t</i> <sup>-3</sup> | 1.46 <i>t</i> <sup>-3</sup> | 1.16 <i>t</i> <sup>-2</sup> | 1.56 <i>t</i> <sup>-6</sup>  |
| 1.03 <i>t</i> <sup>6</sup>  | 2.41 <i>t</i> <sup>3</sup>  | 1.01 <i>t</i> <sup>2</sup>    | 7.47 <i>t</i>               | 2.42 <i>t</i>               | 1.00                        | 9.61 <i>t</i> <sup>-2</sup> | 3.53 <i>t</i> <sup>-2</sup> | 2.81 <i>t</i> <sup>-2</sup> | 3.77 <i>t</i> <sup>-5</sup>  |
| 1.08 <i>t</i> <sup>7</sup>  | 2.50 <i>t</i> <sup>4</sup>  | 1.05 <i>t</i> <sup>3</sup>    | 7.77 <i>t</i> <sup>2</sup>  | 2.52 <i>t</i> <sup>2</sup>  | 1.04 <i>t</i>               | 1.00                        | 3.67 <i>t</i> <sup>-1</sup> | 2.93 <i>t</i> <sup>-1</sup> | 3.93 <i>t</i> <sup>-4</sup>  |
| 2.93 <i>t</i> <sup>7</sup>  | 6.81 <i>t</i> <sup>4</sup>  | 2.87 <i>t</i> <sup>3</sup>    | 2.12 <i>t</i> <sup>3</sup>  | 6.86 <i>t</i> <sup>2</sup>  | 2.83 <i>t</i>               | 2.72                        | 1.00                        | 7.97 <i>t</i> <sup>-1</sup> | 1.07 <i>t</i> <sup>-3</sup>  |
| 3.67 <i>t</i> <sup>7</sup>  | 6.79 <i>t</i> <sup>4</sup>  | 3.60 <i>t</i> <sup>3</sup>    | 2.66 <i>t</i> <sup>3</sup>  | 8.61 <i>t</i> <sup>2</sup>  | 3.55 <i>t</i>               | 3.42                        | 1.25                        | 1.00                        | 1.34 <i>t</i> <sup>-3</sup>  |
| 2.74 <i>t</i> <sup>10</sup> | 7.37 <i>t</i> <sup>7</sup>  | 2.68 <i>t</i> <sup>6</sup>    | 1.98 <i>t</i> <sup>6</sup>  | 6.42 <i>t</i> <sup>5</sup>  | 2.65 <i>t</i> <sup>4</sup>  | 2.55 <i>t</i> <sup>3</sup>  | 9.36 <i>t</i> <sup>2</sup>  | 7.46 <i>t</i> <sup>2</sup>  | 1.00                         |

**The First Law of Thermodynamics.** When a falling weight coils a spring to which it is attached, the weight develops work and the spring absorbs it. Work is *transferred* from the weight to the spring. Similarly heat is transferred from a hot body to a contiguous cold one. When a quantity of work is expended against friction it is *transformed* into an equal quantity of heat, the work and the heat being measured in the same unit. In processes such as these work and heat may indeed be interconverted, but taken together they are neither created nor destroyed. Let us then consider the assumption that work and heat (measured in the same unit), however they may be transferred from body to body and transformed into each other, are not thereby changed in total amount.



Let any body traverse any closed path of change of its thermodynamic state, thus regaining its initial state. The cyclic process serves as a means of transforming the work and heat received by the body into the work and heat given out by it. If  $W_c$  and  $Q_c$  are the algebraic sums of the quantities of work and of heat absorbed by the body, the result is to create the quantity  $W_c + Q_c$  of work and heat if this sum be negative, or to destroy this quantity if the sum be positive. Continued repetition of the process would effect boundless creation or destruction of work or heat or both. Under our assumption, then, we shall have

$$W_c + Q_c = 0. \quad (1)$$

To express the assumption in more convenient form, let  $W_1, Q_1$  be the total work and heat absorbed by the body on any selected path of change of thermodynamic state from any state  $a$  to any other state  $b$ ; let  $W_2, Q_2$  be the work and heat absorbed on any other path of the change of state; and let  $W_3, Q_3$  be the quantities absorbed on any possible path of the reversed change from  $b$  to  $a$ . Then the first path followed by the third, and the second path followed by the third, are closed paths, for which the equation (1) requires that

$$\begin{aligned}(W_1 + Q_1) + (W_3 + Q_3) &= 0, \\ (W_2 + Q_2) + (W_3 + Q_3) &= 0.\end{aligned}$$

It follows that

$$W_1 + Q_1 = W_2 + Q_2,$$

which means that *the algebraic sum of the work and heat absorbed by a body in any change of its thermodynamic state is independent of the path of the change of state*. This principle is termed the *first law of thermodynamics*. Since it is justified by the extended and exact agreement of its consequences with experience, it is to be regarded as an experimentally established truth. It is not a consequence of any theory; it is an *experimental fact*.

**The Energy Law.** From the first law it follows immediately that the sum of the work and heat absorbed by a body in a change of its thermodynamic state is equal to the concurrent change of value of a function of the independent variables that are employed to determine the states. This function is termed