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volume 2

THERMODYNAMICS

P. T. LANDSBERG

THERMODYNAMICS

WITH QUANTUM STATISTICAL ILLUSTRATIONS

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Preface

Many excellent textbooks on thermodynamics are available. They appeal by the simplicity of their fundamental concepts: temperature and heat are familiar from everyday life. Concepts like heat capacity and latent heat are remembered from our school days, and it is reassuring to the readers of such texts to see that these quantities can be measured by accurate methods which are, however, simple in principle. Nevertheless, although it is only rarely emphasized, thermodynamics is among the most abstract branches of physics.

There are two main reasons for this. First, the theory contains results which are within wide limits independent of particular systems. Equations of state, appropriate to special substances, are injected into the framework from experiment or from extra-thermodynamic theories. Secondly, in so far as equilibrium states are concerned, space and time coordinates enter only in a rudimentary manner. Space coordinates occur merely implicitly to describe boundaries between parts of systems which are often homogeneous. Time ordering enters through the principle of the increase of entropy, but, for the greater part, it is not involved at all. Thermodynamics is in fact a study of general relations which refer to an abstract multidimensional phase space, and, in so far as the time coordinate is absent, nothing *happens* in thermodynamics. The *quasistatic process*, for example, is strictly speaking a curve in this phase space, the term *process* being merely a reminder that actual physical processes can often be made to follow such a curve to a high degree of approximation. The abstract nature of the subject is always allowed to become fully evident in this book, and it differs therefore materially from existing texts. For a discussion of these differences the reader is referred to Appendix A.

The scope of the book is strictly limited. Classical, non-relativistic thermodynamics is discussed, and, as the main application, simple systems of weakly interacting particles are treated. On the

other hand, more than usual attention is devoted to these, and statistical mechanics is developed and used to reveal alternative interpretations and applications of the thermodynamic treatment. It is hoped that the reader will in this way grasp some of the crucial points in the relationship between thermodynamics and statistical mechanics. Although the available space is divided evenly between these two topics; this is primarily a book on thermodynamics, so that general principles rather than detailed applications or physical mechanisms are emphasized.

This text should be suitable for anyone who is not deterred by abstract thought. It is self-contained, but a newcomer should not think that it can introduce him to more than one facet of the subject. For instance, questions of historical detail and of experimental results are omitted, as these are adequately discussed elsewhere. It is hoped therefore that this book will supplement existing texts, and contribute something to our understanding of thermodynamics, and to the exposition of its principles.

Many questions under survey in this book have been discussed over a period of years with members of the Natural Philosophy Department of the University of Aberdeen. In particular, acknowledgement must be made of stimulating discussions with Drs F. Ansbacher, E. W. Elcock, D. M. Findlayson, and especially with Dr. C. W. McCombie. I am grateful to Dr. S. C. Nyburg, Keele, for helpful comments on the first few sections. I am indebted also to Professor M. Fierz, from whose profound understanding of thermodynamics I have profited through correspondence, and to Professor M. Born for first encouraging the writing of this book.

P. T. L.

Contents

I. GENERAL THEORY - The First Law	1
1. Nature and Scope of Thermodynamics	1
2. Explanatory Remarks about the Method of Partitions and Enclosures	4
3. Conceptual Tools: Partitions	8
4. The Zeroth Law of Thermodynamics	12
5. The Empirical Temperature	14
6. Conceptual Tools: Phase Space and the Set of Points α	20
7. A Restricted Form of the First Law and the Quantitative Measure of Heat	23
8. Generalizations: Energy and the Set of Points β	29
II. GENERAL THEORY - The Second Law	35
9. Quasistatic Processes	35
10. The 'Interior' (γ) of a Set of Points β	45
11. The Connection between Quasistatic Adiabatic Accessibility and the Existence of an Integrating Factor for $d'Q$ in a Set γ	50
12. The Existence of an Entropy and an Absolute Temperature Function	53
13. The Extent to which Certain Arbitrary Choices can Affect the Properties of Entropy and Absolute Temperature	64
14. The Changes of Entropy in Non-Static Adiabatic Processes	77
15. Survey of Physical Processes	90
III. GENERAL THEORY - The Third Law	96
16. Deducible Properties of the Hypersurface $T = 0$	96
17. The Boundary of Sets β : Unattainability Principles	99
18. Entropy Properties Engendered by the Unattainability of the Absolute Zero	104
19. Axiomatics	105
IV. BASIC APPLICATIONS AND EXTENSIONS	121
20. The Empirical Determination of Entropy and Absolute Temperature Scales from Quasistatic Processes in Special Systems	121
21. 'Simple' Systems: The Extension of Thermodynamics to Open and Non-Equilibrium Systems	128

22. Compound Systems	143
23. Application to Chemical Thermodynamics: The Properties of Phases	162
24. Additional Thermodynamic Functions and their Properties	159
25. Thermodynamic Cycles, and Principles Associated with their Study	170
26. The Ideal Classical Gas	184
27. The Ideal Quantum Gas	201

V. COMBINATIONS OF THERMODYNAMICS AND STATISTICAL MECHANICS	217
28. Statistical Mechanics of the Ideal Gases: General Theory	217
29. Density of States Formulae; Black-Body Radiation	250
30. Non-Black-Body Radiation	291
31. Statistical Mechanics of the Ideal Quantum Gases: Special Topics	306
32. Paramagnetics: Systems Having Two Sets γ Contained in One Set β	329
33. Descriptions which are Intermediate between Thermodynamics and Statistical Mechanics: Temperature-Dependent Energy Levels	343
34. Relations among Statistical Mechanical Principles using the Method of Transition Probabilities	356
35. Thermodynamics as a Precursor of Quantum Mechanics	372

APPENDICES

A. Comments on the Mode of Treatment Adopted	381
B. The Reduction of Pfaffians to Canonical form	392
C. Two Basic Results in Statistical Mechanics	401
D. The Continuous Spectrum Approximation in the Theory of the Quantum Gases	425
E. The Use of the Canonical Distribution in the Theory of the Quantum Gases	432
F. The Method of the Enumeration of States and Most Probable Distributions in the Theory of the Quantum Gases	445
G. Discussion of the Master Equation	463

BIBLIOGRAPHY	476
-------------------------------	------------

AUTHOR INDEX	481
-------------------------------	------------

SUBJECT INDEX	485
--------------------------------	------------

CHAPTER I

General Theory - The First Law

§ 1. Nature and Scope of Thermodynamics

Thermodynamics is the study which seeks to establish quantitative relationships among the macroscopic variables which describe an arbitrary physical system, when this system is in any one of a large number of equilibrium states, the system being very large compared with atomic dimensions. Thus unless the contrary is explicitly stated, as in the study of surface tension phenomena for instance, surface effects can be neglected compared with volume effects. Thermodynamics also seeks to establish relationships between the values of the variables which specify initial and final equilibrium states of a system which is interacting with another system. Some remarks will elucidate this definition.

(a) The macroscopic variables include quantities like pressure, volume, molecular concentrations and the like, which can all be measured by known methods. They may also include electrical and magnetic variables and possibly some specific thermodynamic quantities. The existence and properties of these latter quantities are to be discussed in the present chapter, and for our purposes it is therefore convenient to assume that the use of typically thermodynamic quantities has been avoided in the specification of thermodynamic states. At the same time, typically microscopic information, such as the occupation probabilities of quantum states, is not needed for thermodynamics. It is assumed in our definition that one can normally agree on what constitutes a suitable set of macroscopic variables for a physical system in a given group of equilibrium states.

(b) Since the physical system under investigation must undergo certain changes when its thermodynamic properties are studied, one must also agree on the domain of permissible changes. For example, if a gas is confined to a cylinder with an adjustable piston, one may call this a system S . If the piston is moved, one

will normally regard this modification as a state of the system S , rather than as a state of an entirely new system T . On the other hand, if the piston is removed completely, so that the gas can escape into a larger volume, one may or may not regard the resulting arrangement as belonging to a new system. Thus, one carries along with the idea of a physical system the assumption that it can be modified within certain defined limits.

(c) When a system, together with its domain of permissible changes, has been specified in ordinary language, and a set of values for its thermodynamic variables has also been chosen, one can ask another person to set up copies of this system for which these variables have the same values, within certain tolerances, which must also be specified. One can now ask a third person to attempt to find a macroscopic difference between these systems (other than their location in space and time), by making arbitrary measurements to the agreed accuracy. If he succeeds in finding a macroscopic difference, one includes the value of the variable measured by him in the specification of the first system, so that this value must now also be exhibited by the copies of the system. The third person is now again asked to find a difference. By repeating this procedure, a situation is eventually attained such that the systems under consideration have to be regarded as macroscopically similar by any third observer. One then says that one has arrived at a macroscopic specification of the *state* of the first system.

(d) Our definition presumes also that agreement can be obtained on what constitutes an equilibrium state. It used to be said that an equilibrium state is one in which the physical variables of the system are all constant in time. But we now know that the fluctuations which these variables undergo under normal conditions can in fact never be removed. So it would be better to look for the absence of systematic trends in the time averages of the physical variables involved (over times judged as 'reasonable'). The times required may be very large when the systematic changes which are suspected are very slow, and this has created difficulties in the past, for instance in connection with the third law of thermodynamics, for states which are not true

equilibrium states. However, the science of thermodynamics has grown up precisely because it is normally possible to make convenient conventions on what one is to regard as necessary macroscopic variables, as permissible changes of a system, as equilibrium states, and so on.

Another complication must be borne in mind. Suppose one is cooling a certain mass of water, so that one has at one time ice and water in equilibrium, and at another time only ice. It is clear that the variable specifying the amount of water present may be redundant. If the permissible changes of the system include the vaporization of the water and the dissociation of the water molecules, then the variable specifying the number of hydrogen and oxygen molecules present may sometimes be required, and sometimes be redundant. The macroscopic variables of real interest to be associated with a physical system will therefore depend on what one might call the *approximate* state of the system ('ice only' or 'ice and water' for example). Having specified that state, it will always be possible to give a maximum number, n say, of independent macroscopic variables which define the equilibrium state of the system uniquely. It is clear that the nature of these variables, and their number, depend in general on the *approximate* state of the system. It will depend in addition on personal preference, since alternative sets of independent variables will in general be available. But n must satisfy $n \geq 2$ (see § 19, p. 119). We shall call macroscopic variables which can enter into the specification of an equilibrium state simply *thermodynamic variables*, and the state a *thermodynamic state*.

By regarding the thermodynamic variables of a system as coordinate axes of an n -dimensional space, one can picture an equilibrium state of a system as represented by a point in the appropriate *phase space*. This concept will be discussed in greater detail (§ 6, p. 20).

Since the nature of the thermodynamic variables, and their number, can vary within wide limits, the basic theoretical framework of thermodynamics must be kept very general. This has the advantage of giving the theory a wide range of application; but this is balanced by the drawback that thermodynamic

reasoning is in general unsuitable for giving insight into the *details* of physical processes.

This last observation, together with the remark that thermodynamics leaves microscopic variables on one side, leads to the conclusion that a thermodynamic theory is necessarily incomplete. For any system to which thermodynamics can be applied, a deeper-going theory should exist which yields insight into the detailed physical processes involved.

This deeper theory must also give some account of the nature of equilibrium states, and therefore of fluctuation phenomena; and, of course, it must lead to the thermodynamics of the system. Such theories are provided by statistical mechanics. Since a statistical mechanical theory must exist for every system to which thermodynamics can be applied, it follows that the whole of thermodynamics should in fact be deducible from statistical mechanics, if the latter is formulated in a sufficiently general way. This presents very interesting problems. They are briefly outlined in § 34 and Appendix C, but they are not our primary concern.

§ 2. Explanatory Remarks About the Method of Partitions and Enclosures

The basic concepts of thermodynamics (temperature, p. 14, and quantity of heat, p. 24) will be introduced in what the reader may well regard as a rather obtuse manner. The treatment of these concepts forms a clearly defined part of this book, and begins in the following section. It is therefore appropriate to explain in this section the reason for this mode of treatment, which differs from that usually followed. Since the present section is purely explanatory, and can be omitted as far as the logical development of the subject is concerned, we shall allow ourselves one luxury here, on the understanding that it shall not be indulged in elsewhere. This luxury is the free use of concepts like temperature and thermal energy, of which we believe the reader to have a good intuitive understanding, *but which have not yet been formally introduced.*

Such a procedure follows in fact the usual lines of a first approach to any scientific subject. One is aware of certain general and qualitative features of one's surroundings, and uses ordinary words to describe these. It is in order to *sharpen* one's understanding of these concepts, not to *create* them, that formal definitions are required. Often these are not easy to construct. Unsuspected difficulties are encountered and, as they are removed one by one, a truer understanding is gained of the phenomena with which one is dealing. Thus a relatively crude use of words is introductory to a more sophisticated language.

This idea can be put alternatively in the form of a paradox, which is liable to confront an author who is expounding a deductive system. On the one hand, his aim will be to introduce concepts formally and rigorously when the development of the theory has reached the appropriate point. On the other hand, if the imagination of a reader is to be captured sufficiently, so as to encourage him to read on, the author's objectives must be discussed in terms of the crude concepts at various points when the more precise ideas are not yet available. The paradox consists of the author's inability to follow both courses of action at the same time.

There are various forms of energy: kinetic, thermal, chemical, electromagnetic, etc. Suppose we have full knowledge of the properties of all forms of energy, except just one. We shall call this the x -form for short. Suppose also that we know most about the a -form of energy. One should then naturally try and give an account of the x -form in terms of the a -form of energy. In order to achieve this in a logically satisfactory manner, it will be convenient to introduce two devices.* The first device enables one to feed the a -form of energy into the system, but it prevents all other forms of energy from passing into it. One will arrange things in such a manner that, in the system, the a -form is *completely transformed* into the x -form of energy. If the x -form of energy is in fact mechanical energy, then a fixed amount can be supplied in different ways, using forces and displacements of various magnitudes. Thus our first device, which can be pictured as a special kind of enclosure, can be used to investigate what different methods of supplying the a -form of energy exist, such that all methods take the enclosed system from a fixed state 1 to a fixed state 2. Let us label the different methods of sup-

* These devices are endowed with extraordinary properties. According to Professor M. Fierz, Wolfgang Pauli used to refer to these as *Zaubermittel*.

plying a -energy in this series of tests by the index m . One can then also ask how the total amount of a -energy supplied, $W_{12}(m)$ say, depends on the method m used to supply it. If one finds that $W_{12}(m)$ is independent of m in all series of such tests, one might for instance, subject to additional assumptions which need not concern us here, infer the existence of a useful function of state, f say. With every state, 1, 2, \dots , i , \dots say, of the system is associated a number $f(i)$ such that, in a series of tests as described,

$$f(i) - f(j) = W_{ji}(m) \quad \text{for all } m$$

This would be an important step in the explanation of the x -form of energy in terms of the a -form of energy, since the function $f(i)$ occurs in the theory of the x -form and the a -form, and the function $W_{ji}(m)$ occurs *only* in the theory of the a -form.

These remarks are intended to smooth the path for the introduction of the adiabatic partition (p. 10), when the a -form of energy is mechanical energy and the x -form is thermal energy.

The usefulness of the second device can be seen as follows. The mechanical equilibrium between gases may be investigated by placing the gases into two compartments of a fixed enclosure which allows no energy to pass through it. The compartments are separated by a sliding partition which moves until equal pressures are exerted on either side of it: it transmits mechanical energy, but no other form of energy. The elementary laws of the mechanical equilibrium of fluids can be investigated with the aid of this device. One learns, for instance, that the two part-systems cannot be in mechanical equilibrium with each other if the variables which define their respective states have arbitrary values. Instead, the moving partition, which effects a mechanical coupling between the two part-systems, forces one new relation (pressure equality) on all the variables involved. Similarly, the simplest laws which govern the equilibrium with regard to the x -form of energy or, more simply expressed, which govern x -equilibrium, can be investigated by means of a partition which transmits the x -form of energy only. This supplements the first device, which does not transmit x -energy, but does transmit a -energy. One would be justified in saying that this device effects

a form of x -coupling, and one would expect x -equilibrium to impose a new relation on all the variables involved. Reading 'thermal' for ' x ' it will be found on p. 15 that this relation can be regarded as temperature equality.

The remarks above are intended to smooth the path for the introduction of the diathermic partition (p. 11).

If one takes the view that all forms of energy, except one, are understood, one is thus led to the introduction of the two devices mentioned, and one may expect to attain some understanding of the unknown form in terms of the known forms. It would of course be inconsistent to take the view just indicated of thermal energy in the development of thermodynamics, and to take the same view of electromagnetic energy in the development of electromagnetic theory. The view is tenable only if, in an encyclopaedia of all the physical sciences, it is taken with respect to one form of energy only.

That this point of view should be adopted in thermodynamics rather than in any other branch of physics, is historically conditioned. After all, it was in the study of thermal phenomena that the very notion of energy was first conceived in full generality.* However, it was not clearly appreciated at the time that energy in other than mechanical and thermal forms can exist. It is the existence of these other forms of energy which makes some of the statements of a well formulated science of thermodynamics somewhat more involved than was appreciated by the earlier authors. But the existence of these other forms of energy is of little importance for the immediate task. This is to give definitions, as well as generalizations from experiment, which enable one to show how the notion of thermal energy can be evolved from that of mechanical energy, and how the notion of a function of state known as temperature can also be introduced. This leads to the apparent obtuseness of the present approach which has been referred to above.

* The possibility of converting energy of position into energy of motion was of course known well before the general energy principle was understood. The latter can perhaps be associated with H. von Helmholtz's paper *On the conservation of force* (1847).

It would indeed be much simpler to use immediately the assumption that a temperature function exists, and that equality between temperatures is necessary and sufficient for thermal equilibrium. This procedure is also quite satisfactory, but it is appropriate only if one is prepared to omit a logical analysis of the basic thermodynamic concepts.

This logical analysis is at the present state of our knowledge basic to the whole subject. In the first place, as has already been remarked, it is only with the aid of these partitions that the increments * of heat $d'Q$ and of mechanical work $d'W$ can be clearly distinguished, thus creating the basis for the first and second laws of thermodynamics. In the second place, these partitions are essential for what might be called the *basic trick* in thermodynamic arguments. This trick is to envisage a non-equilibrium situation, say a temperature gradient in a system. One then supposes that the insertion of a large number of adiabatic walls (which do not allow heat to pass) into this system does not affect its properties, except that the temperature gradient can now be maintained indefinitely. In this way the non-equilibrium situation has been converted to an equilibrium situation, and thermodynamics may be applied: It is only by virtue of this basic trick that one can talk about the entropy of non-equilibrium states of a system; hence this idea enables one to make statements such as 'the entropy of an isolated system tends to increase', for this statement implies that the entropy concept can be applied to non-equilibrium situations.

In this way one can avoid Kirchhoff's objection† to Planck's early writings on thermodynamics. Kirchhoff argued that the entropy concept is defined only for *reversible* processes (these are referred to as *quasistatic* processes in this book). He therefore considered that it cannot be used for *irreversible* (here: *non-static*) processes.

§ 3. Conceptual Tools: Partitions

The discussion of the relationships among the equilibrium states of a system is greatly facilitated by the introduction of partitions.

* See p. 24 for an explanation of the notation.

† Planck, M, *Naturwissenschaften*, 33, 231 (1946).

For the present purpose an *ideal partition* is an object O with the following properties: (a) it is infinitely thin; (b) when inserted into a system which is in equilibrium, it does not change this equilibrium state; (c) an equilibrium system exists which is divided into two parts by O such that, upon withdrawal of O , the two part-systems attain new equilibrium states. Conditions (a) and (b) ensure that a partition has no extraneous effects upon any idealized experiment under discussion. For instance, a wall whose sole purpose is to separate two chemically reacting species, should obviously not be made of radioactive material whose decay products might change the chemical composition of these chemical species. Condition (b) is intended to rule out such devices.

We shall sometimes speak simply of *partitions* (without the prefix *ideal*). In such situations we insist merely on condition (c), but not on conditions (a) and (b). A partition is then merely any object which can prevent the attainment of thermodynamic equilibrium between the systems which it separates.

Though an ideal partition does not exist, one can arrange real partitions in an ordered series, whose individual items approach the properties of an ideal partition ever more closely. A statement about a hypothetical experiment which involves an ideal partition can therefore be tested by performing the corresponding real experiment with each item of the ordered series of real partitions, and extrapolating the results obtained to what one would expect to find with an ideal partition. It will be assumed throughout that a connection can always be found between ideal and real partitions by performing this type of limiting process.

A great variety of physically quite distinct partitions are covered by the above definition. Two particular examples will now be specified more closely.

(A) An enclosure F does not allow the exchange of mass with the outside, and changes in long-range forces (electric, magnetic, gravitational) which act on F from the outside are kept negligible. An arbitrary physical system K is placed inside F and is allowed to attain an equilibrium state e . F is said to be adiabatic in the restricted sense,* if K remains in equilibrium, unless mechanical

* A summary of the properties of such partitions is given in Table 8.1, p. 30.

changes are produced in K by movements of parts of the enclosure F (or by transmission through the walls of F).

Suppose now that a mechanical change is produced in the system K by movement of the enclosure F , with the result that K attains a new equilibrium state ϵ' . The process linking ϵ and ϵ' is then said to be *adiabatic in the restricted sense*. The states ϵ and ϵ' are said to be *linked by a process which is adiabatic in a restricted sense*. The idea of linkage does not express a definite sense of direction for the change. If ϵ can be taken into ϵ' or if ϵ' can be taken into ϵ , we shall in both cases regard these states as linked by the process under consideration.

It follows that the mechanical operation of stirrers and pistons which act on the system is allowed in a restricted adiabatic process. Any other change which is brought about by a combination of mechanical and non-mechanical methods, or by non-mechanical methods only, or which involves an exchange of mass, or a change in the long-range forces, is not adiabatic in the restricted sense.

(B) Consider again the enclosure F which is adiabatic in the restricted sense. During the experiment to be described, however, no mechanical work shall be transmitted through it, and the changes in the long-range forces which act on F must again be negligibly small. Suppose the space inside F is divided into two parts by an ideal partition G . The area of G is in intimate contact with an ideal partition H , which is adiabatic in the restricted sense. Let two physical systems K_1 , K_2 , whose sets of thermodynamic variables are denoted by x_1 , x_2 respectively, be in equilibrium in the two spaces. Assume that neither system contains or is enclosed by partitions, apart from the container F , whose sole purpose is to ensure complete isolation of the system and to prevent an exchange of mass between the system and its surroundings. The systems are otherwise arbitrary. Let ϵ_1 , ϵ_2 be the equilibrium states of K_1 and K_2 . After the withdrawal of H let the new equilibrium states be ϵ'_1 , ϵ'_2 respectively. It will be required of G that it does not allow the exchange of mass, mechanical energy, electricity or electromagnetic radiation. Also, whatever (within certain limits) the initial states ϵ_1 and