CHAPTER 1

INTRODUCTION

The science of thermodynamics, in the widest sense in which the word is used nowadays, may be said to be concerned with the understanding and interpretation of the properties of matter in so far as they are affected by changes of temperature. In this sense thermodynamics ranks as one of the major subdivisions of physical science, and a variety of mathematical and experimental techniques may be invoked to aid its advancement, with the ultimate aim of providing an explanation of the observed properties of matter at all temperatures in terms of its atomic constitution and the forces exerted by atoms upon one another. This statement covers perhaps a wider field of investigation than can legitimately be called thermodynamics. For example, it can hardly be claimed that the theory of the chemical forces which bind together the atoms of stable chemical compounds is a branch of thermodynamics; rather is it a branch of quantum mechanics in which the concept of temperature plays no part. On the other hand, as soon as we become interested in the excitation or dissociation of molecules as a consequence of heating, the matter becomes truly one in which thermodynamical considerations are involved. In the same way the existence of solids and a great many properties of solids which are only to a minor degree affected by temperature may be explained satisfactorily as purely mechanical consequences of the forces between atoms; thermodynamics strictly enters only when we attempt to account for the temperature-dependent properties, such as heat capacity and (in certain solids) magnetic susceptibility. And, of course, the study of phase transitions (solid to liquid, liquid to gas, or changes of crystalline structure) is in its essence thermodynamical, and provides indeed some of the most interesting problems of present-day thermodynamics.

This is the wide use of the term, but there is a narrower sense in which it is used, and this is what may conveniently be distinguished as classical thermodynamics, the subject of this book. Here the method of approach takes no account of the atomic constitution of matter, but seeks rather to derive from certain basic postulates, the laws of thermodynamics, relations between the observed properties of substances. In contrast to the atomic theory of thermal phenomena, classical thermodynamics makes no attempt to provide a mechanistic explanation of why a given substance has the properties observed experimentally; its function is to link together the many observable properties so that they can all be seen to be a consequence of a few. For
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example, if the equation of state of a gas (the relation between its pressure, volume and temperature) be known, and a determination made of its specific heat at constant pressure over a range of temperatures, then by thermodynamical arguments the specific heat at constant volume may be found, as well as the dependence of both specific heats on pressure or volume. In addition, it may be predicted whether the gas will be heated or cooled when it is expanded through a throttle from a high to a low pressure, and the magnitude of the temperature change may be calculated precisely. This is a comparatively elementary example of the application of classical thermodynamics to a physical problem. The applications discussed in this book should give some idea of the power of thermodynamics to deal with a considerable variety of phenomena, but to appreciate the full scope of the method, and to see how much can be achieved by the use of only simple mathematics, reference should be made to more detailed treatises on the subject. There is none which encompasses the whole field, for the applications of thermodynamics range over many branches of physics, chemistry and engineering, and in each are so extensive as to demand separate treatment if anything like completeness is to be attained. Nevertheless, in spite of a great diversity of methods of presentation, the ideas involved are exactly the same in principle.

The two approaches to thermodynamical theory, the classical or phenomenological approach on the one hand and the statistical approach through molecular dynamics on the other, are so different that it is worth discussing the relationship between them, especially as we shall have no more concern with the latter in what follows. The laws of thermodynamics were arrived at as a consequence of observation and generalization of experience; continued application of the methods of classical thermodynamics to practical problems showed these laws to predict the correct answer in all cases. This is the empirical justification for regarding the laws as having a very wide range of validity. But classical thermodynamics makes no attempt to explain why the laws have their particular form, that is, to exhibit the laws as a necessary consequence of other laws of physics which may be regarded as even more fundamental. This is one of the problems which is treated by statistical thermodynamics. From a consideration of the behaviour of a large assembly of atoms, molecules or other physical entities, it may be shown, with a fair degree of rigour (enough to satisfy most physicists but few pure mathematicians), that those properties of the assembly which are observable by macroscopic measurements are related in obedience with the laws of thermodynamics. This result, which is not derived by considering any very specific model, but which has as wide a range of validity as the laws of mechanics themselves, has perhaps tended to encourage an under-
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valuation of classical thermodynamics. For from the point of view of the physicist who aims to penetrate as far as possible into the deepest mysteries of the physical world, and to find the fundamental principles from which all physical laws derive, thermodynamics has ceased to be an interesting study, since it is wholly contained within the laws of dynamics.

Not all practitioners, however, of the physical sciences (in which term we may include without prejudice chemists and engineers) have this particular ambition to probe the ultimate mysteries of their craft, and many who have are forced by circumstances to forgo their desire. For these, the great majority, thermodynamics is not so obviously a trivial pursuit; indeed, in many branches it is an almost indispensable tool. For often enough in the pure sciences, and still more in the applied sciences, it is more important to know the relations between the properties of substances than to have a clear understanding of the origin of these properties in terms of the molecular constitution. And even the theoretical physicist who is concerned with a detailed explanation of these properties may find classical thermodynamics a valuable aid, since it reduces the number of problems which require separate statistical treatment—once certain results have been derived the rest follow thermodynamically, as will become clearer in later chapters.

These are some of the reasons which make a study of classical thermodynamics a valuable part of the education of a physical scientist, but there is another, less purely practical reason. The development of the ideas in thermodynamics has a formal elegance which is exceedingly satisfying aesthetically. It has not perhaps quite the rigour of a perfect mathematical proof, but it approaches nearer that logical ideal than almost any other branch of natural science. For this reason alone it may be regarded as an important part of the education of a scientist.

Because classical thermodynamics is capable of so rigorous a formulation it is desirable, in the author’s opinion, to present at least the early steps of the argument in a way which brings out the logical development clearly. At the same time a wholly mathematical approach may prove either repellent to the student, or, what is worse, formally intelligible and yet meaningless in terms of physical reality. The early chapters which follow therefore represent some sort of a compromise in which the ideas are expressed in as unmathematical a form as is consistent with exactitude. By the use of more mathematics the arguments could be shortened on paper; it is doubtful whether such a treatment would lead to a speedier assimilation of the ideas by any but the most mathematically minded students.

The pursuit of rigour involves almost inevitably abandoning the
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historical approach. Great ideas are more often arrived at by a combination of intuition and a judicious disregard of niceties than by a systematic and logical development of explicitly formulated premises, and certainly the history of thermodynamics bears out this view. But once the goal has been attained it is possible to go back over the road and see how the same end could have been reached more logically. While it is fascinating for the historian of science to see how Carnot, in his astonishing memoir *Sur la puissance motrice du feu* (1824), arrived at so many correct conclusions after having started with the incorrect caloric theory of heat, only confusion would result from trying to base a modern treatment on this work. Carnot’s main results were reproduced and extended, principally by James and William Thomson, Clausius and Rankine, after the experiments of Joule (about 1843–9) had provided convincing evidence for interpreting heat as a form of energy and had thus extended the law of conservation of energy to include thermal processes. Even this work, however, suffers from a number of defects from the point of view of logical presentation. For example, it is undesirable in a purely phenomenological development to have recourse to an unobservable atomic interpretation of the nature of heat, if it can be avoided, as it can; and secondly, there is little explicit discussion in this early work of the meaning of that all-important term *temperature*. To be sure, our bodily senses allow us to comprehend with ease the idea of temperature, and without such direct apprehension the development of thermodynamics would surely have been considerably retarded. But that is no reason for continuing to regard the idea of temperature as essentially intuitive, if a satisfactory definition of the term can be given which does not rely on our qualitative sensory impressions only.

We therefore begin our formal treatment of the subject by showing how the ideas of temperature and heat may be systematically formulated on the basis of experiment, so that the subsequent development may be as free as possible from the suspicion that it is based on intuitive concepts or atomistic interpretations.
CHAPTER 2

THE ZEROTH AND FIRST LAWS
OF THERMODYNAMICS

Fundamental definitions

Thermodynamics is concerned with real physical systems, which may be solid or fluid, or mixtures of both, or even an evacuated space containing nothing but electromagnetic radiation. Usually the system considered must be contained within a vessel of some kind with which it does not react chemically.

Now the walls of different vessels differ considerably in the ease with which influences from without may be transmitted to the system within. Water within a thin-walled glass flask may have its properties readily changed by holding the flask over a flame or by putting it in a refrigerator; or the change brought about by the flame may be simulated (though not so easily) by directing an intense beam of radiation on to the flask. If, on the other hand, the water is contained within a double-walled vacuum flask with silvered walls (Dewar vessel), the effects of flame or refrigerator or radiation are reduced almost to nothing. The degree of isolation of the contents from external influences can be varied continuously over such a wide range, that it is not a very daring extrapolation to imagine the existence of a vessel having perfectly isolating walls, so that the substance contained within is totally unaffected by any external agency.† Such an ideal wall is termed an adiabatic wall, and a substance wholly contained within adiabatic walls is said to be isolated. Walls which are not adiabatic are diathermal walls. Two physical systems separated from each other only by diathermal walls are said to be in thermal contact.

An adiabatic wall may be so nearly realized in practice that it may be claimed to be a matter of experience that when a physical system is entirely enclosed within adiabatic walls it tends towards,

† It is perhaps too much of an extrapolation to imagine the walls impervious to gravitational fields. Rather than postulate the existence of such a wall we shall for the moment avoid problems involving gravitation. It is hoped that when, later in the book, we make occasional reference to gravitational fields the reader will feel enough confidence in his physical understanding of thermodynamics to be able to ignore lacunae in the basic formulation. If he cannot overcome his scruples he must work out a better treatment for himself.
and eventually reaches, a state in which no further change is perceptible, no matter how long one waits. The system is then said to be in equilibrium.

Mechanical systems exhibit a number of different types of static equilibrium, which may be exemplified by the behaviour of a spherical ball resting on curves of different shapes and acted upon by gravity. Thermodynamic systems show analogies to some of these, and it is convenient to point them out at this stage, although it is not strictly pertinent to the argument and, indeed, necessitates the use of concepts which have not yet been defined. The following discussion should therefore be regarded as an explanatory parenthesis only. Stable equilibrium may be represented by a ball resting at the bottom of a valley; the equilibrium of a pure gas at rest at a uniform temperature is analogous to this. There is no realizable thermodynamic analogue to unstable equilibrium,† as of a ball poised at the top of a hill. A ball resting on a flat plane is in neutral equilibrium; so is a mixture of water and water vapour enclosed in a cylinder and subjected to a constant pressure by means of a frictionless piston, the whole being maintained at such a temperature that the vapour pressure of the water is exactly equal to the pressure exerted by the piston. For just as the ball may remain at rest at any point on the plane, so the proportion of liquid and vapour may be adjusted at will by movement of the piston. Finally, there is metastable equilibrium, represented by a ball resting in a local depression at the top of a hill, and stable with respect to small displacements while unstable with respect to large displacements. It is difficult to find a strict thermodynamic analogue to this type of metastability, but perhaps the nearest approach is exemplified by a supercooled vapour or by a mixture of hydrogen and oxygen. Both the systems have the appearance of stability and may be subjected to small variations of pressure and temperature as if they were truly stable; yet the effect of a condensation nucleus on the former or a spark on the latter shows clearly that they have not the stability of, say, helium gas in equilibrium. The analogy with the ball in metastable equilibrium is not perfect, for these thermodynamic systems are never strictly in equilibrium. Given long enough a supercooled vapour will eventually condense of its own accord, and given long enough a mixture of hydrogen and oxygen will transform itself into water. The time involved may be so enormous, however, perhaps $10^{100}$ years or more, that the process is not perceptible. For most purposes, provided the rapid change is not artificially stimulated, the systems may be regarded as being in equilibrium.

Although we may discover analogies between thermodynamic and simple mechanical systems it is well to bear in mind an important

† See p. 111 for further discussion of this point.


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difference. The equilibrium of a thermodynamic system is never static; the ‘matter of experience’ mentioned above, that systems tend to a state from which they subsequently do not change, is not strictly an experimental truth. A microscopic examination of minute particles suspended in a fluid reveals them to be in a state of continuous agitation (Brownian movement), and in the same way delicate measurements on a gas would reveal that the density at a given point is subject to incessant minute fluctuations about its mean value. This is, of course, a consequence of the rapid motions of the molecules composing the system, and is an intrinsic property of the system. If one were prepared to wait long enough, and in most cases long enough means a time enormously longer than the age of the universe, one might observe really sizeable departures from the average state of the system. For example, there is no reason why 1 c.c. of a gas, in a state of complete thermal isolation, should not spontaneously contract to half its volume, leaving the other half of the vessel evacuated, and just as suddenly revert to its average state of virtually uniform density. But the whole fluctuation would take only about $10^{-4}$ sec. to be accomplished, and might be expected to occur once in about $10^{10^4}$ years, so that the possibility of making such an observation need not be seriously contemplated. For most purposes it is quite satisfactory to imagine an isolated system to tend to a definite and invariant state of equilibrium, and classical thermodynamics assumes the equilibrium state to have this static property. In so far as this assumption is not strictly true we must expect to have to revise any results we may derive before applying them to problems in which fluctuations play a significant part. We shall return to this point later (Chapter 7).

Temperature

At this stage it is convenient to consider an especially simple type of thermodynamic system in order to arrive at an idea of the meaning of temperature, and we shall for the present confine our attention to homogeneous fluids, either liquids or gases. A gas, of course, of its very nature fills its containing vessel; we imagine any liquid under consideration to be contained exactly by its vessel, leaving no free space for vapour. The especial simplicity of a fluid derives from the fact that its shape is of no consequence thermodynamically; deformation of the containing vessel, if unaccompanied by any change in volume, may in principle be accomplished without the performance of work, and does not alter the thermal properties of the fluid within. By contrast, a solid body can only be altered in shape by the application of considerable stresses, and the thermal properties are in general affected in the process.
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It is a fact of experience that a given mass of fluid in equilibrium is completely specified (apart from its shape which is, as just pointed out, of no significance) by a prescription of its volume, $V$, and pressure, $P$.† If we take a certain quantity of gas, enclosed in a cylinder with a movable piston, we may fix the volume at some predetermined value and then, with the help of such well-known auxiliary devices as an oven and a refrigerator, set about altering the pressure to any required value. It may readily be verified by experiment that whatever the process by which the pressure and volume are adjusted, the final state of the gas is always the same, no matter what property is examined (e.g. colour, smell, sensation of warmth, thermal conductivity, viscosity, etc.). That is to say, any property capable of quantitative measurement may be expressed as a function of the two variables, $P$ and $V$.

Let us consider now the behaviour of two systems which are not thermally isolated from one another. If we take two isolated systems and allow them to come into equilibrium separately, and then bring them into thermal contact by replacing the adiabatic wall which divides them by a diathermal wall, we shall find in general that changes take place in both, until eventually the composite system attains a new state of equilibrium, in which the two separate systems are said to be in equilibrium with one another. As a matter of sensory experience we know that this is because two systems chosen independently will not in general have the same temperature, and the changes which occur when they are brought into thermal contact result in their eventually attaining the same temperature. But there is no need at this stage to employ the, as yet, meaningless word temperature to describe this particular fact of experience. It is sufficient to realize that two systems may be separately in equilibrium and yet not in equilibrium with one another. In particular, two given masses of fluid are not in equilibrium with one another if their pressures and volumes (the parameters of state) are chosen arbitrarily. Of the four variables of the composite system, $P_1$ and $V_1$ for the first fluid, and $P_2$ and $V_2$ for the second, three may be fixed arbitrarily, but for the two fluids to be in equilibrium with one another the fourth variable is then determined by the other three. One may, for example, adjust both $P_1$ and $V_1$ by placing the first fluid in an oven until the required values are reached; if then $V_2$ is fixed it will be found necessary to adjust $P_2$ by placing the second fluid in the oven before the two fluids are in equilibrium with one another. This may be expressed in a formal manner by saying that for two given masses of fluid there exists a function of the variables of state.

† We leave out of consideration for the moment the possible influences of electric and magnetic fields on the properties of the fluid, assuming such fields to be absent.
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\[ F(P_1, V_1, P_2, V_2) \] such that when the fluids are in equilibrium with one another,

\[ F(P_1, V_1, P_2, V_2) = 0. \]  \hspace{1cm} (2.1)

The form of the function will depend of course on the fluids considered, and may be determined, if required, by a sufficient number of experiments which measure the conditions under which the fluids are in equilibrium.

In order to establish the existence of the important property temperature it is necessary to demonstrate that (2.1) may always be rewritten in the form

\[ \phi_1(P_1, V_1) = \phi_2(P_2, V_2), \]  \hspace{1cm} (2.2)

in which the variables describing the two systems are separated. This we shall do first by a formal mathematical argument, and then (since to many students the mathematical argument appears too abstract to be altogether meaningful) by an equivalent argument in terms of hypothetical experiments. Both arguments depend on a further fact of experience which has come to be regarded as sufficiently important to be designated the zeroth law of thermodynamics:

If, of three bodies, A, B and C, A and B are separately in equilibrium with C, then A and B are in equilibrium with one another.

It is also desirable, for reasons which will appear later, to state what is essentially the converse of the zeroth law:

If three or more bodies are in thermal contact, each to each, by means of diathermal walls, and are all in equilibrium together, then any two taken separately are in equilibrium with one another.

The sort of simple experiment upon which the zeroth law is based may be illustrated by the following example. Let C be a mercury-in-glass thermometer, in which the mercury is a fluid at roughly zero pressure (if the thermometer is evacuated) and with a volume determined by its height in the tube; the height of the mercury in a given thermometer is sufficient to determine its state. Then according to the zeroth law if the reading of the thermometer is the same when it is immersed in two different liquids, A and B, nothing will happen when A and B are placed in thermal contact. It is easy enough to multiply examples of the application of this law, which expresses so elementary and common an experience that it was not formulated until long after the first and second laws had been thoroughly established.

Consider now three fluids, A, B and C. The conditions under which A and C are in equilibrium may be expressed by the equation

\[ F_1(P_A, V_A, P_C, V_C) = 0, \]
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which may be solved for $P_C$ to give an equation of the form

$$P_C = f_2(P_A, V_A, V_C).$$  \hspace{1cm} \text{(2-3)}

Similarly, the conditions under which $B$ and $C$ are in equilibrium may be expressed by the equation

$$F_3(P_B, V_B, P_C, V_C) = 0,$$

or, again by solving for $P_C$,

$$P_C = f_3(P_B, V_B, V_C).$$ \hspace{1cm} \text{(2-4)}

Hence the conditions under which $A$ and $B$ are separately in equilibrium with $C$ may be expressed, from (2-3) and (2-4), by the equation

$$f_1(P_A, V_A, V_C) = f_2(P_B, V_B, V_C).$$ \hspace{1cm} \text{(2-5)}

But if $A$ and $B$ are separately in equilibrium with $C$, then according to the zeroth law they are in equilibrium with one another, so that (2-5) must be equivalent to an equation of the form

$$F_3(P_A, V_A, P_B, V_B) = 0.$$  \hspace{1cm} \text{(2-6)}

It will be seen now that while (2-5) contains the variable $V_C$, (2-6) does not. If the two equations are to be equivalent, it can only mean that the functions $f_1$ and $f_2$ contain $V_C$ in such a form that it cancels out on the two sides of (2-5) [e.g. $f_1(P_A, V_A, V_C)$ might take the form

$$\phi_1(P_A, V_A) \xi(V_C) + \eta(V_C)].$$

When this cancellation is performed, (2-5) will have the form of (2-2),

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B),$$

and by an obvious extension of the argument

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B) = \phi_3(P_C, V_C),$$

and so on for any number of fluids in equilibrium with one another. We have thus demonstrated that for every fluid it is possible to find a function $\phi(P, V)$ of its parameters of state (different of course for each fluid) which has the property that the numerical value of $\phi (\text{=} \theta$, say) is the same for all fluids in equilibrium with one another. The quantity $\theta$ is called the empirical temperature, and the equation

$$\phi(P, V) = \theta$$  \hspace{1cm} \text{(2-7)}

is called the equation of state of the fluid. In this way we have shown, by means of the zeroth law, that there exists a function of the state of a fluid, the temperature, which has the property of taking the same