

CHAPTER I  
HEAT AS A MODE OF MOTION

Most of modern physics and chemistry is based on three fundamental ideas: first, matter is made of atoms and molecules, very small and very numerous; second, it is impossible in principle to observe details of atomic and molecular motions below a certain scale of smallness; and third, heat is mechanical motion of the atoms and molecules, on such a small scale that it cannot be completely observed. The first and third of these ideas are products of the last century, but the second, the uncertainty principle, the most characteristic result of the quantum theory, has arisen since 1900. By combining these three principles, we have the theoretical foundation for studying the branches of physics dealing with matter and chemical problems.

**1. The Conservation of Energy.**—From Newton's second law of motion, one can prove immediately that the work done by an external force on a system during any motion equals the increase of kinetic energy of the system. This can be stated in the form

$$KE_2 - KE_1 = \int_1^2 dW, \quad (1.1)$$

where  $KE$  stands for the kinetic energy,  $dW$  the infinitesimal element of work done on the system. Certain forces are called conservative; they have the property that the work done by them when the system goes from an initial to a final state depends only on the initial and final state, not on the details of the motion from one state to the other. Stated technically, we say that the work done between two end points depends only on the end points, not on the path. A typical example of a conservative force is gravitation; a typical nonconservative force is friction, in which the longer the path, the greater the work done. For a conservative force, we define the potential energy as

$$PE_1 = -\int_0^1 dW. \quad (1.2)$$

This gives the potential energy at point 1, as the negative of the work done in bringing the system from a certain state 0 where the potential energy is zero to the state 1, an amount of work which depends only on the points 1 and 0, not on the path. Then we have

$$\int_1^2 dW = -PE_2 + PE_1, \quad (1.3)$$

and, combining with Eq. (1.1),

$$KE_1 + PE_1 = KE_2 + PE_2 = E, \quad (1.4)$$

where, since 1 and 2 are arbitrary points along the path and  $KE + PE$  is the same at both these points, we must assume that  $KE + PE$  remains constant, and may set it equal to a constant  $E$ , the total energy. This is the law of conservation of energy.

To avoid confusion, it is worth while to consider two points connected with the potential energy: the negative sign which appears in the definition (1.2), and the choice of the point where the potential energy is zero. Both points can be illustrated simply by the case of gravity acting on bodies near the earth. Gravity acts down. We may balance its action on a given body by an equal and opposite upward force, as by supporting the body by the hand. We may then define the potential energy of the body at height  $h$  as the work done by this balancing force in raising the body through this height. Thus if the mass of the body is  $m$ , and the acceleration of gravity  $g$ , the force of gravity is  $-mg$  (positive directions being upward), the balancing force is  $+mg$ , and the work done by the hand in raising the mass through height  $h$  is  $mgh$ , which we define as the potential energy. The negative sign, then, comes because the potential energy is defined, not as the work done by the force we are interested in, but the work done by an equal and opposite balancing force. As for the arbitrary position where we choose the potential energy to be zero, that appears in this example because we can measure our height  $h$  from any level we choose. It is important to notice that the same arbitrary constant appears essentially in the energy  $E$ . Thus, in Eq. (1.4), if we chose to redefine our zero of potential energy, we should have to add a constant to the total energy at each point of the path. Another way of stating this is that it is only the difference  $E - PE$  whose magnitude is determined, neither the total energy nor the potential energy separately. For  $E - PE$  is the kinetic energy, which alone can be determined by direct experiment, from a measurement of velocities.

Most actual forces are not conservative; for in almost all practical cases there is friction of one sort or another. And yet the last century has seen the conservation of energy built up so that it is now regarded as the most important principle of physics. The first step in this development was the mechanical theory of heat, the sciences of thermodynamics and statistical mechanics. Heat had for many years been considered as a fluid, sometimes called by the name caloric, which was abundant in hot bodies and lacking in cold ones. This theory is adequate to explain calorimetry, the science predicting the final temperature if substances of different initial temperatures are mixed. Mixing a cold body, lacking in caloric, with a hot one, rich in it, leaves the mixture with a medium

amount of heat, sufficient to raise it to an intermediate temperature. But early in the nineteenth century, difficulties with the theory began to appear. As we look back, we can see that these troubles came from the implied assumption that the caloric, or heat, was conserved. In a calorimetric problem, some of the caloric from the hot body flows to the cold one, leaving both at an intermediate temperature, but no caloric is lost. It was naturally supposed that this conservation was universal. The difficulty with this assumption may be seen as clearly as anywhere in Rumford's famous observation on the boring of cannon. Rumford noticed that a great deal of heat was given off in the process of boring. The current explanation of this was that the chips of metal had their heat capacity reduced by the process of boring, so that the heat which was originally present in them was able to raise them to a higher temperature. Rumford doubted this, and to demonstrate it he used a very blunt tool, which hardly removed any chips at all and yet produced even more heat than a sharp tool. He showed by his experiments beyond any doubt that heat could be produced continuously and in apparently unlimited quantity, by the friction. Surely this was impossible if heat, or caloric, were a fluid which was conserved. And his conclusion stated essentially our modern view, that heat is really a form of energy, convertible into energy. In his words:<sup>1</sup>

What is Heat? Is there any such thing as an igneous fluid? Is there any thing that can with propriety be called caloric? . . . In reasoning on this subject, we must not forget to consider that most remarkable circumstance, that the source of Heat generated by friction, in these Experiments, appeared evidently to be inexhaustible.

It is hardly necessary to add, that any thing which any insulated body, or system of bodies, can continue to furnish without limitation, cannot possibly be a material substance; and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of any thing, capable of being excited and communicated, in the manner the Heat was excited and communicated in these experiments, except it be MOTION.

From this example, it is clear that both conservation laws broke down at once. In a process involving friction, energy is not conserved, but rather disappears continually. At the same time, however, heat is not conserved, but appears continually. Rumford essentially suggested that the heat which appeared was really simply the energy which had disappeared, observable in a different form. This hypothesis was not really proved for a good many years, however, until Joule made his experiments on the mechanical equivalent of heat, showing that when a certain amount of work or mechanical energy disappears, the amount of heat

<sup>1</sup> Quoted from W. F. Magie, "Source Book in Physics," pp. 160-161, McGraw-Hill Book Company, Inc., 1935.

appearing is always the same, no matter what the process of transformation may be. The caloric, formerly considered as a unit for measuring the amount of caloric present, was seen to be really a unit of energy, convertible into ergs, the ordinary units of energy. And it became plain that in a process involving friction, there really was no loss of energy. The mechanical energy, it is true, decreased, but there was an equal increase in what we might call thermal energy, or heat energy, so that the total energy, if properly defined, remained constant. This generalization was what really established the conservation of energy as a great and important principle. Having identified heat as a form of energy, it was only natural for the dynamical theory of heat to be developed, in which heat was regarded as a mode of motion of the molecules, on such a small scale that it could not be observed in an ordinary mechanical way. The extra kinetic and potential energy of the molecules on account of this thermal motion was identified with the energy which had disappeared from view, but had reappeared to be measured as heat. With the development of thermodynamics and kinetic theory, conservation of energy took its place as the leading principle of physics, which it has held ever since.

**2. Internal Energy, External Work, and Heat Flow.**—We have seen that the theory of heat is based on the idea of conservation of energy, on the assumption that the total energy of the universe is conserved, if we include not only mechanical energy but also the mechanical equivalent of the heat energy. It is not very convenient to talk about the whole universe every time we wish to work a problem, however. Ordinarily, thermodynamics deals with a finite system, isolated from its neighbors by an imaginary closed surface. Everything within the surface belongs to the system, everything outside is excluded. Usually, though not always, a fixed amount of matter belongs to the system during the thermodynamic processes we consider, no matter crossing the boundary. Very often, however, we assume that energy, in the form of mechanical or thermal energy, or in some other form, crosses the boundary, so that the energy of the system changes. The principle of conservation, which then becomes equivalent to the first law of thermodynamics, simply states that the net increase of energy in the system, in any process, equals the energy which has flowed in over the boundary, so that no energy is created within the system. To make this a precise law, we must consider the energy of the body and its change on account of flow over the boundary of the system.

The total energy of all sorts contained within the boundary of the system is called the internal energy of the system, and is denoted by  $U$ . From an atomic point of view, the internal energy consists of kinetic and potential energies of all the atoms of the system, or carrying it

further, of all electrons and nuclei constituting the system. Since potential energies always contain arbitrary additive constants, the internal energy  $U$  is not determined in absolute value, only differences of internal energy having a significance, unless some convention is made about the state of zero internal energy. Macroscopically (that is, viewing the atomic processes on a large scale, so that we cannot see what individual atoms are doing), we do not know the kinetic and potential energies of the atoms, and we can only find the change of internal energy by observing the amounts of energy added to the system across the boundary, and by making use of the law of conservation of energy. Thermodynamics, which is a macroscopic science, makes no attempt to analyze internal energy into its parts, as for example mechanical energy and heat energy. It simply deals with the total internal energy and with its changes.

Energy can enter the system in many ways, but most methods can be classified easily and in an obvious way into mechanical work and heat. Familiar examples of external mechanical work are work done by pistons, shafts, belts and pulleys, etc., and work done by external forces acting at a distance, as gravitational work done on bodies within the system on account of gravitational attraction by external bodies. A familiar example of heat flow is heat conduction across the surface. Convection of heat into the system is a possible form of energy interchange if atoms and molecules are allowed to cross the surface, but not otherwise. Electric and magnetic work done by forces between bodies within the system and bodies outside is classified as external work; but if the electromagnetic energy enters in the form of radiation from a hot body, it is classified as heat. There are cases where the distinction between the two forms of transfer of energy is not clear and obvious, and electromagnetic radiation is one of them. In ambiguous cases, a definite classification can be obtained from the atomic point of view, by means of statistical mechanics.

In an infinitesimal change of the system, the energy which has entered the system as heat flow is called  $dQ$ , and the energy which has left the system as mechanical work is called  $dW$  (so that the energy which has entered as mechanical work is called  $-dW$ ). The reason for choosing this sign for  $dW$  is simply convention; thermodynamics is very often used in the theory of heat engines, which produce work, so that the important case is that in which energy leaves the system as mechanical work, or when  $dW$  in our definition is positive. We see then that the total energy which enters the system in an infinitesimal change is  $dQ - dW$ . By the law of conservation of energy, the increase in internal energy in a process equals the energy which has entered the system:

$$dU = dQ - dW. \quad (2.1)$$

Equation (2.1) is the mathematical statement of the first law of thermodynamics. It is to be noted that both sides of the equation should be expressed in the same units. Thus if internal energy and mechanical work are expressed in ergs, the heat absorbed must be converted to ergs by use of the mechanical equivalent of heat,

$$1 \text{ calorie} = 4.185 \times 10^7 \text{ ergs} = 4.185 \text{ joules.}$$

Or if the heat absorbed is to be measured in calories, the work and internal energy should be converted into that unit.

It is of the utmost importance to realize that the distinction between heat flow and mechanical work, which we have made in talking about energy in transit into a system, does not apply to the energy once it is in the system. It is completely fallacious to try to break down the statement of Eq. (2.1) into two statements: "The increase of heat energy of a body equals the heat which has flowed in," and "The decrease of mechanical energy of a body equals the work done by the body on its surroundings." For these statements would correspond just to separate conservation laws for heat and mechanical energy, and we have seen in the last section that such separate laws do not exist. To return to the last section, Rumford put a great deal of mechanical work into his cannon, produced no mechanical results on it, but succeeded in raising its temperature greatly. As we have stated before, the energy of a system cannot be differentiated or separated into a mechanical and a thermal part, by any method of thermodynamics. The distinction between heat and work is made in discussing energy in transit, and only there.

The internal energy of a system depends only on the state of the system; that is, on pressure, volume, temperature, or whatever variables are used to describe the system uniquely. Thus, the change in internal energy between two states 1 and 2 depends only on these states. This change of internal energy is an integral,

$$U_2 - U_1 = \int_1^2 dU = \int_1^2 dQ - \int_1^2 dW. \quad (2.2)$$

Since this integral depends only on the end points, it is independent of the path used in going from state 1 to state 2. But the separate integrals

$$\int_1^2 dQ \quad \text{and} \quad \int_1^2 dW,$$

representing the total heat absorbed and the total work done in going from state 1 to 2, are not independent of the path, but may be entirely different for different processes, only their difference being independent of path. Since these integrals are not independent of the path, they cannot be written as differences of functions  $Q$  and  $W$  at the end points, as  $\int dU$  can be written as the difference of the  $U$ 's at the end points.

Such functions  $Q$  and  $W$  do not exist in any unique way, and we are not allowed to use them.  $W$  would correspond essentially to the negative of the potential energy, but ordinarily a potential energy function does not exist. Similarly  $Q$  would correspond to the amount of heat in the body, but we have seen that this function also does not exist. The fact that functions  $Q$  and  $W$  do not exist, or that  $\int dQ$  and  $\int dW$  are not independent of path, really is only another way of saying that mechanical and heat energy are interchangeable, and that the internal energy cannot be divided into a mechanical and a thermal part by thermodynamics.

At first sight, it seems too bad that  $\int dQ$  is not independent of path, for some such quantity would be useful. It would be pleasant to be able to say, in a given state of the system, that the system had so and so much heat energy. Starting from the absolute zero of temperature, where we could say that the heat energy was zero, we could heat the body up to the state we were interested in, find  $\int dQ$  from absolute zero up to this state, and call that the heat energy. But the stubborn fact remains that we should get different answers if we heated it up in different ways. For instance, we might heat it at an arbitrary constant pressure until we reached the desired temperature, then adjust the pressure at constant temperature to the desired value; or we might raise it first to the desired pressure, then heat it at that pressure to the final temperature; or many other equally simple processes. Each would give a different answer, as we can easily verify. There is nothing to do about it.

It is to avoid this difficulty, and obtain something resembling the "amount of heat in a body," which yet has a unique meaning, that we introduce the entropy. If  $T$  is the absolute temperature, and if the heat  $dQ$  is absorbed at temperature  $T$  in a reversible way, then  $\int dQ/T$  proves to be an integral independent of path, which evidently increases as the body is heated; that is, as heat flows into it. This integral, from a fixed zero point (usually taken to be the absolute zero of temperature), is called the entropy. Like the internal energy, it is determined by the state of the system, but unlike the internal energy it measures in a certain way only heat energy, not mechanical energy. We next take up the study of entropy, and of the related second law of thermodynamics.

**3. The Entropy and Irreversible Processes.**—Unlike the internal energy and the first law of thermodynamics, the entropy and the second law are relatively unfamiliar. Like them, however, their best interpretation comes from the atomic point of view, as carried out in statistical mechanics. For this reason, we shall start with a qualitative description of the nature of the entropy, rather than with quantitative definitions and methods of measurement.

The entropy is a quantity characteristic of the state of a system, measuring the randomness or disorder in the atomic arrangement of that

state. It increases when a body is heated, for then the random atomic motion increases. But it also increases when a regular, orderly motion is converted into a random motion. Thus, consider an enclosure containing a small piece of crystalline solid at the absolute zero of temperature, in a vacuum. The atoms of the crystal are regularly arranged and at rest; its entropy is zero. Heat the crystal until it vaporizes. The molecules are now located in random positions throughout the enclosure and have velocities distributed at random. Both types of disorder, in the coordinates and in the velocities, contribute to the entropy, which is now large. But we could have reached the same final state in a different way, not involving the absorption of heat by the system. We could have accelerated the crystal at the absolute zero, treating it as a projectile and doing mechanical work, but without heat flow. We could arrange a target, so that the projectile would automatically strike the target, without external action. If the mechanical work which we did on the system were equivalent to the heat absorbed in the other experiment, the final internal energy would be the same in each case. In our second experiment, then, when the projectile struck the target it would be heated so hot as to vaporize, filling the enclosure with vapor, and the final state would be just the same as if the vaporization were produced directly. The increase of entropy must then be the same, for by hypothesis the entropy depends only on the state of the system, not on the path by which it has reached that state. In the second case, though the entropy has increased, no heat has been absorbed. Rather, ordered mechanical energy (the kinetic energy of the projectile as a whole, in which each molecule was traveling at the same velocity as every other) has been converted by the collision into random, disordered energy. Just this change results in an increase of entropy. It is plain that entropy cannot be conserved, in the same sense that matter, energy, and momentum are. For here entropy has been produced or created, just by a process of changing ordered motion into disorder.

Many other examples of the two ways of changing entropy could be given, but the one we have mentioned illustrates them sufficiently. We have considered the increase of entropy of the system; let us now ask if the processes can be reversed, and if the entropy can be decreased again. Consider the first process, where the solid was heated gradually. Let us be more precise, and assume that it was heated by conduction from a hot body outside; and further that the hot body was of an adjustable temperature, and was always kept very nearly at the same temperature as the system we were interested in. If it were just at the same temperature, heat would not flow, but if it were always kept a small fraction of a degree warmer, heat would flow from it into the system. But that process can be effectively reversed. Instead of having the outside body a fraction

of a degree warmer than the system, we let it be a fraction of a degree cooler, so that heat will flow out instead of in. Then things will cool down, until finally the system will return to the absolute zero, and everything will be as before. In the direct process heat flows into the system; in the inverse process it flows out, an equal amount is returned, and when everything is finished all parts of the system and the exterior are in essentially the same state they were at the beginning. But now try to reverse the second process, in which the solid at absolute zero was accelerated, by means of external work, then collided with a target, and vaporized. The last steps were taken without external action. To reverse it, we should have the molecules of the vapor condense to form a projectile, all their energy going into ordered kinetic energy. It would have to be as shown in a motion picture of the collision run backward, all the fragments coalescing into an unbroken bullet. Then we could apply a mechanical brake to the projectile as it receded from the target, and get our mechanical energy out again, with reversal of the process. But such things do not happen in nature. The collision of a projectile with a target is essentially an irreversible process, which never happens backward, and a reversed motion picture of such an event is inherently ridiculous and impossible. The statement that such events cannot be reversed is one of the essential parts of the second law of thermodynamics. If we look at the process from an atomic point of view, it is clear why it cannot reverse. The change from ordered to disordered motion is an inherently likely change, which can be brought about in countless ways; whereas the change from disorder to order is inherently very unlikely, almost sure not to happen by chance. Consider a jigsaw puzzle, which can be put together correctly in only one way. If we start with it put together, then remove each piece and put it in a different place on the table, we shall certainly disarrange it, and we can do it in almost countless ways; while if we start with it taken apart, and remove each piece and put it in a different place on the table, it is true that we may happen to put it together in the process, but the chances are enormously against it.

The real essence of irreversibility, however, is not merely the strong probability against the occurrence of a process. It is something deeper, coming from the principle of uncertainty. This principle, as we shall see later, puts a limit on the accuracy with which we can regulate or prescribe the coordinates and velocities of a system. It states that any attempt to regulate them with more than a certain amount of precision defeats its own purpose: it automatically introduces unpredictable perturbations which disturb the system, and prevent the coordinates and velocities from taking on the values we desire, forcing them to deviate from these values in an unpredictable way. But this just prevents us from being able experimentally to reverse a system, once the randomness

has reached the small scale at which the principle of uncertainty operates. To make a complicated process like a collision reverse, the molecules would have to be given very definitely determined positions and velocities, so that they would just cooperate in such a way as to coalesce and become unbroken again; any errors in determining these conditions would spoil the whole thing. But we cannot avoid these errors. It is true that by chance they may happen to fall into line, though the chance is minute. But the important point is that we cannot do anything about it.

From the preceding examples, it is clear that we must consider two types of processes: reversible and irreversible. The essential feature of reversible processes is that things are almost balanced, almost in equilibrium, at every stage, so that an infinitesimal change will swing the motion from one direction to the other. Irreversible processes, on the other hand, involve complete departure from equilibrium, as in a collision. It will be worth while to enumerate a few other common examples of irreversible processes. Heat flow from a hot body to a cold body at more than an infinitesimal difference of temperature is irreversible, for the heat never flows from the cold to the hot body. Another example is viscosity, in which regular motion of a fluid is converted into random molecular motion, or heat. Still another is diffusion, in which originally unmixed substances mix with other, so that they cannot be unmixed again without external action. In all these cases, it is possible of course to bring the system itself back to its original state. Even the projectile which has been vaporized can be reconstructed, by cooling and condensing the vapor and by recasting the material into a new projectile. But the surroundings of the system would have undergone a permanent change; the energy that was originally given the system as mechanical energy, to accelerate the bullet, is taken out again as heat, in cooling the vapor, so that the net result is a conversion of mechanical energy into heat in the surroundings of the system. Such a conversion of mechanical energy into heat is often called degradation of energy, and it is characteristic of irreversible processes. A reversible process is one which can be reversed in such a way that the system itself and its surroundings both return to their original condition; while an irreversible process is one such that the system cannot be brought back to its original condition without requiring a conversion or degradation of some external mechanical energy into heat.

4. The Second Law of Thermodynamics.—We are now ready to give a statement of the second law of thermodynamics, in one of its many forms: The entropy, a function only of the state of a system, increases in a reversible process by an amount equal to  $dQ/T$  (where  $dQ$  is the heat absorbed,  $T$  the absolute temperature at which it is absorbed) and increases by a larger amount than  $dQ/T$  in an irreversible process.

This statement involves a number of features. First, it gives a way of calculating entropy. By sufficient ingenuity, it is always possible to find reversible ways of getting from any initial to any final state, provided both are equilibrium states. Then we can calculate  $\int dQ/T$  for such a reversible path, and the result will be the change of entropy between the two states, an integral independent of path. We can then measure entropy in a unique way. If we now go from the same initial to the same final state by an irreversible path, the change of entropy must still be the same, though now  $\int dQ/T$  must necessarily be smaller than before, and hence smaller than the change in entropy. We see that the heat absorbed in an irreversible path must be less than in a reversible path between the same end points. Since the change in internal energy must be the same in either case, the first law then tells us that the external work done by the system is less for the irreversible path than for the reversible one. If our system is a heat engine, whose object is to absorb heat and do mechanical work, we see that the mechanical work accomplished will be less for an irreversible engine than for a reversible one, operating between the same end points.

It is interesting to consider the limiting case of adiabatic processes, processes in which the system interchanges no heat with the surroundings, the only changes in internal energy coming from mechanical work. We see that in a reversible adiabatic process the entropy does not change (a convenient way of describing such processes). In an irreversible adiabatic process the entropy increases. In particular, for a system entirely isolated from its surroundings, the entropy increases whenever irreversible processes occur within it. An isolated system in which irreversible processes can occur is surely not in a steady, equilibrium state; the various examples which we have considered are the rapidly moving projectile, a body with different temperatures at different parts (to allow heat conduction), a fluid with mass motion (to allow viscous friction), a body containing two different materials not separated by an impervious wall (to allow diffusion). All these systems have less entropy than the state of thermal equilibrium corresponding to the same internal energy, which can be reached from the original state by irreversible processes without interaction with the outside. This state of thermal equilibrium is one in which the temperature is everywhere constant, there is no mass motion, and where substances are mixed in such a way that there is no tendency to diffusion or flow of any sort. A condition for thermal equilibrium, which is often applied in statistical mechanics, is that the equilibrium state is that of highest entropy consistent with the given internal energy and volume.

These statements concerning adiabatic changes, in which the entropy can only increase, should not cause one to forget that in ordinary changes,

in which heat can be absorbed or rejected by the system, the entropy can either increase or decrease. In most thermodynamic problems, we confine ourselves to reversible changes, in which the only way for the entropy to change is by heat transfer.

We shall now state the second law in a mathematical form which is very commonly used. We let  $S$  denote the entropy. Our previous statement is then  $dS \geq dQ/T$ , or  $T dS \geq dQ$ , the equality sign holding for the reversible, the inequality for irreversible, processes. But now we use the first law, Eq. (2.1), to express  $dQ$  in terms of  $dU$  and  $dW$ . The inequality becomes at once

$$T dS \geq dU + dW, \quad (4.1)$$

the mathematical formulation of the second law. For reversible processes, which we ordinarily consider, the equality sign is to be used.

The second law may be considered as a postulate. We shall see in Chap. II that definite consequences can be drawn from it, and they prove to be always in agreement with experiment. We notice that in stating it, we have introduced the temperature without apology, for the first time. This again can be justified by its consequences: the temperature so defined proves to agree with the temperature of ordinary experience, as defined for example by the gas thermometer. Thermodynamics is the science that simply starts by assuming the first and second laws, and deriving mathematical results from them. Both laws are simple and general, applying as far as we know to all sorts of processes. As a result, we can derive simple, general, and fundamental results from thermodynamics, which should be independent of any particular assumptions about atomic and molecular structure, or such things. Thermodynamics has its drawbacks, however, in spite of its simplicity and generality. In the first place, there are many problems which it simply cannot answer. These are detailed problems relating, for instance, to the equation of state and specific heat of particular types of substances. Thermodynamics must assume that these quantities are determined by experiment; once they are known, it can predict certain relationships between observed quantities, but it is unable to say what values the quantities must have. In addition to this, thermodynamics is limited to the discussion of problems in equilibrium. This is on account of the form of the second law, which can give only qualitative, and not quantitative, information about processes out of equilibrium.

Statistical mechanics is a much more detailed science than thermodynamics, and for that reason is in some ways more complicated. It undertakes to answer the questions, how is each atom or molecule of the substance moving, on the average, and how do these motions lead to observable large scale phenomena? For instance, how do the motions

of the molecules of a gas lead to collisions with a wall which we interpret as pressure? Fortunately it is possible to derive some very beautiful general theorems from statistical mechanics. In fact, one can give proofs of the first and second laws of thermodynamics, as direct consequences of the principles of statistical mechanics, so that all the results of thermodynamics can be considered to follow from its methods. But it can go much further. It can start with detailed models of matter and work through from them to predict the results of large scale experiments on the matter. Statistical mechanics thus is much more powerful than thermodynamics, and it is essentially just as general. It is somewhat more complicated, however, and somewhat more dependent on the exact model of the structure of the material which we use. Like thermodynamics, it is limited to treating problems in equilibrium.

Kinetic theory is a study of the rates of atomic and molecular processes, treated by fairly direct methods, without much benefit of general principles. If handled properly, it is an enormously complicated subject, though simple approximations can be made in particular cases. It is superior to statistical mechanics and thermodynamics in just two respects. In the first place, it makes use only of well-known and elementary methods, and for that reason is somewhat more comprehensible at first sight than statistical mechanics, with its more advanced laws. In the second place, it can handle problems out of equilibrium, such as the rates of chemical reactions and other processes, which cannot be treated by thermodynamics or statistical mechanics.

We see that each of our three sciences of heat has its own advantages. A properly trained physicist or chemist should know all three, to be able to use whichever is most suitable in a given situation. We start with thermodynamics, since it is the most general and fundamental method, taking up thermodynamic calculations in the next chapter. Following that we treat statistical mechanics, and still later kinetic theory. Only then shall we be prepared to make a real study of the nature of matter.



## CHAPTER II

## THERMODYNAMICS

In the last chapter, we became acquainted with the two laws of thermodynamics, but we have not seen how to use them. In this chapter, we shall learn the rules of operation of thermodynamics, though we shall postpone actual applications until later. It has already been mentioned that thermodynamics can give only qualitative information for irreversible processes. Thus, for instance, the second law may be stated

$$dW \leq T dS - dU, \quad (1)$$

giving an upper limit to the work done in an irreversible process, but not predicting its exact amount. Only for reversible processes, where the equality sign may be used, can thermodynamics make definite predictions of a quantitative sort. Consequently almost all our work in this chapter will deal with reversible systems. We shall find a number of differential expressions similar to Eq. (1), and by proper treatment we can convert these into equations relating one or more partial derivatives of one thermodynamic variable with respect to another. Such equations, called thermodynamic formulas, often relate different quantities all of which can be experimentally measured, and hence furnish a check on the accuracy of the experiment. In cases where one of the quantities is difficult to measure, they can be used to compute one of the quantities from the others, avoiding the necessity of making the experiment at all. There are a very great many thermodynamic formulas, and it would be hopeless to find all of them. But we shall go into general methods of computing them, and shall set up a convenient scheme for obtaining any one which we may wish, with a minimum of computation.

Before starting the calculating of the formulas, we shall introduce several new variables, combinations of other quantities which prove to be useful for one reason or another. As a matter of fact, we shall work with quite a number of variables, some of which can be taken to be independent, others dependent, and it is necessary to recognize at the outset the nature of the relations between them. In the next section we consider the equation of state, the empirical relation connecting certain thermodynamic variables.

**1. The Equation of State.**—In considering the properties of matter, our system is ordinarily a piece of material enclosed in a container and

subject to a certain hydrostatic pressure. This of course is a limited type of system, for it is not unusual to have other types of stresses acting, such as shearing stresses, unilateral tensions, and so on. Thermodynamics applies to as general a system as we please, but for simplicity we shall limit our treatment to the conventional case where the only external work is done by a change of volume, acting against a hydrostatic pressure. That is, if  $P$  is the pressure and  $V$  the volume of the system, we shall have

$$dW = P dV. \quad (1.1)$$

In any case, even with much more complicated systems, the work done will have an analogous form; for Eq. (1.1) is simply a force ( $P$ ) times a displacement ( $dV$ ), and we know that work can always be put in such a form. If there is occasion to set up the thermodynamic formulas for a more general type of force than a pressure, we simply set up  $dW$  in a form corresponding to Eq. (1.1), and proceed by analogy with the derivations which we shall give here.

We now have a number of variables:  $P$ ,  $V$ ,  $T$ ,  $U$ , and  $S$ . How many of these, we may ask, are independent? The answer is, any two. For example, with a given system, we may fix the pressure and temperature. Then in general the volume is determined, as we can find experimentally. The experimental relation giving volume as a function of pressure and temperature is called the equation of state. Ordinarily, of course, it is not a simple analytical equation, though in special cases like a perfect gas it may be. Instead of expressing volume as a function of pressure and temperature, we may simply say that the equation of state expresses a relation between these three variables, which may equally well give pressure as a function of temperature and volume, or temperature as a function of volume and pressure. Of these three variables, two are independent, one dependent, and it is immaterial which is chosen as the dependent variable.

The equation of state does not include all the experimental information which we must have about a system or substance. We need to know also its heat capacity or specific heat, as a function of temperature. Suppose, for instance, that we know the specific heat at constant pressure  $C_P$  as a function of temperature at a particular pressure. Then we can find the difference of internal energy, or of entropy, between any two states. From the first state, we can go adiabatically to the pressure at which we know  $C_P$ . In this process, since no heat is absorbed, the change of internal energy equals the work done, which we can compute from the equation of state. Then we absorb heat at constant pressure, until we reach the point from which another adiabatic process will carry us to the desired end point. The change of internal energy can be found for the process at constant pressure, since there we know  $C_P$ , from which we can



find the heat absorbed, and since the equation of state will tell us the work done; for the final adiabatic process we can likewise find the work done and hence the change of internal energy. Similarly we can find the change in entropy between initial and final state. In our particular case, assuming the process to be carried out reversibly, the entropy will not change along the adiabatics, but the change of entropy will be

$$\frac{dQ}{T} = \frac{C_P dT}{T}$$

in the process at constant pressure. We see, in other words, that the difference of internal energy or of entropy between any two states can be found if we know equation of state and specific heat, and since both these quantities have arbitrary additive constants, this is all the information which we can expect to obtain about them anyway.

Given the equation of state and specific heat, we see that we can obtain all but two of the quantities  $P$ ,  $V$ ,  $T$ ,  $U$ ,  $S$ , provided those two are known. We have shown this if two of the three quantities  $P$ ,  $V$ ,  $T$  are known; but if  $U$  and  $S$  are determined by these quantities, that means simply that two out of the five quantities are independent, the rest dependent. It is then possible to use any two as independent variables. For instance, in thermodynamics it is not unusual to use  $T$  and  $S$ , or  $V$  and  $S$ , as independent variables, expressing everything else as functions of them.

**2. The Elementary Partial Derivatives.**—We can set up a number of familiar partial derivatives and thermodynamic formulas, from the information which we already have. We have five variables, of which any two are independent, the rest dependent. We can then set up the partial derivative of any dependent variable with respect to any independent variable, keeping the other independent variable constant. A notation is necessary showing in each case what are the two independent variables. This is a need not ordinarily appreciated in mathematical treatments of partial differentiation, for there the independent variables are usually determined in advance and described in words, so that there is no ambiguity about them. Thus, a notation, peculiar to thermodynamics, has been adopted. In any partial derivative, it is obvious that the quantity being differentiated is one of the dependent variables, and the quantity with respect to which it is differentiated is one of the independent variables. It is only necessary to specify the other independent variable, the one which is held constant in the differentiation, and the convention is to indicate this by a subscript. Thus  $(\partial S/\partial T)_P$ , which is ordinarily read as the partial of  $S$  with respect to  $T$  at constant  $P$ , is the derivative of  $S$  in which pressure and temperature are independent variables. This derivative would mean an entirely different thing from the derivative of  $S$  with respect to  $T$  at constant  $V$ , for instance.

There are a number of partial derivatives which have elementary meanings. Thus, consider the thermal expansion. This is the fractional increase of volume per unit rise of temperature, at constant pressure:

$$\text{Thermal expansion} = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P. \quad (2.1)$$

Similarly, the isothermal compressibility is the fractional decrease of volume per unit increase of pressure, at constant temperature:

$$\text{Isothermal compressibility} = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T. \quad (2.2)$$

This is the compressibility usually employed; sometimes, as in considering sound waves, we require the adiabatic compressibility, the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. If there is no heat flow, the entropy is unchanged, in a reversible process, so that an adiabatic process is one at constant entropy. Then we have

$$\text{Adiabatic compressibility} = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S. \quad (2.3)$$

The specific heats have simple formulas. At constant volume, the heat absorbed equals the increase of internal energy, since no work is done. Since the heat absorbed also equals the temperature times the change of entropy, for a reversible process, and since the heat capacity at constant volume  $C_V$  is the heat absorbed per unit change of temperature at constant volume, we have the alternative formulas

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V. \quad (2.4)$$

To find the heat capacity at constant pressure  $C_P$ , we first write the formula for the first and second laws, in the case we are working with, where the external work comes from hydrostatic pressure and where all processes are reversible:

$$dU = T dS - P dV,$$

or

$$T dS = dU + P dV. \quad (2.5)$$

From the second form of Eq. (2.5), we can find the heat absorbed, or  $T dS$ . Now  $C_P$  is the heat absorbed, divided by the change of temperature, at constant pressure. To find this, we divide Eq. (2.5) by  $dT$ , indicate that the process is at constant  $P$ , and we have

$$C_P = T \left( \frac{\partial S}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P. \quad (2.6)$$

Here, and throughout the book, we shall ordinarily mean by  $C_V$  and  $C_P$  not the specific heats (heat capacities per gram), but the heat capacities of the mass of material with which we are working; though often, where no confusion will arise, we shall refer to them as the specific heats.

From the first and second laws, Eq. (2.5), we can obtain a number of other formulas immediately. Thus, consider the first form of the equation,  $dU = T dS - P dV$ . From this we can at once keep the volume constant (set  $dV = 0$ ), and divide by  $dS$ , obtaining

$$\left(\frac{\partial U}{\partial S}\right)_V = T. \quad (2.7)$$

Similarly, keeping entropy constant, so that we have an adiabatic process, we have

$$\left(\frac{\partial U}{\partial V}\right)_S = -P. \quad (2.8)$$

But we could equally well have used the second form of Eq. (2.5), obtaining

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}. \quad (2.9)$$

From these examples, it will be clear how formulas involving partial derivatives can be found from differential expressions like Eq. (2.5).

**3. The Enthalpy, and Helmholtz and Gibbs Free Energies.**—We notice that Eq. (2.6) for the specific heat at constant pressure is rather complicated. We may, however, rewrite it

$$C_P = \left[\frac{\partial(U + PV)}{\partial T}\right]_P, \quad (3.1)$$

for  $\left[\frac{\partial(PV)}{\partial T}\right]_P = P\left(\frac{\partial V}{\partial T}\right)_P$ , since  $P$  is held constant in the differentiation.

The quantity  $U + PV$  comes in sufficiently often so that it is worth giving it a symbol and a name. We shall call it the enthalpy, and denote it by  $H$ . Thus we have

$$\begin{aligned} H &= U + PV, \\ dH &= dU + P dV + V dP \\ &= T dS + V dP, \end{aligned} \quad (3.2)$$

using Eq. (2.5). From Eq. (3.2), we see that if  $dP = 0$ , or if the process is taking place at constant pressure, the change of the enthalpy equals the heat absorbed. This is the feature that makes the enthalpy a useful quantity. Most actual processes are carried on experimentally at con-

stant pressure, and if we have the enthalpy tabulated or otherwise known, we can very easily find the heat absorbed. We see at once that

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P, \quad (3.3)$$

a simpler formula than Eq. (2.6). As a matter of fact, the enthalpy fills essentially the role for processes at constant pressure which the internal energy does for processes at constant volume. Thus the first form of Eq. (2.5),  $dU = T dS - P dV$ , shows that the heat absorbed at constant volume equals the increase of internal energy, just as Eq. (3.2) shows that the heat absorbed at constant pressure equals the increase of the enthalpy.

In introducing the entropy, in the last chapter, we stressed the idea that it measured in some way the part of the energy of the body bound up in heat, though that statement could not be made without qualification. The entropy itself, of course, has not the dimensions of energy, but the product  $TS$  has. This quantity  $TS$  is sometimes called the bound energy, and in a somewhat closer way it represents the energy bound as heat. In any process, the change in  $TS$  is given by  $T dS + S dT$ . If now the process is reversible and isothermal (as for instance the absorption of heat by a mixture of liquid and solid at the melting point, where heat can be absorbed without change of temperature, merely melting more of the solid),  $dT = 0$ , so that  $d(TS) = T dS = dQ$ . Thus the increase of bound energy for a reversible isothermal process really equals the heat absorbed. This is as far as the bound energy can be taken to represent the energy bound as heat; for a nonisothermal process the change of bound energy no longer equals the heat absorbed, and as we have seen, no quantity which is a function of the state alone can represent the total heat absorbed from the absolute zero.

If the bound energy  $TS$  represents in a sense the energy bound as heat, the remaining part of the internal energy,  $U - TS$ , should be in the same sense the mechanical part of the energy, which is available to do mechanical work. We shall call this part of the energy the Helmholtz free energy, and denote it by  $A$ . Let us consider the change of the Helmholtz free energy in any process. We have

$$\begin{aligned} A &= U - TS, \\ dA &= dU - T dS - S dT. \end{aligned} \quad (3.4)$$

By Eq. (1) this is

$$dA \leq -dW - S dT,$$

or

$$-dA \geq dW + S dT. \quad (3.5)$$

For a system at constant temperature, this tells us that the work done is less than or equal to the decrease in the Helmholtz free energy. The Helmholtz free energy then measures the maximum work which can be done by the system in an isothermal change. For a process at constant temperature, in which at the same time no mechanical work is done, the right side of Eq. (3.5) is zero, and we see that in such a process the Helmholtz free energy is constant for a reversible process, but decreases for an irreversible process. The Helmholtz free energy will decrease until the system reaches an equilibrium state, when it will have reached the minimum value consistent with the temperature and with the fact that no external work can be done.

For a system in equilibrium under hydrostatic pressure, we may rewrite Eq. (3.5) as

$$dA = -P dV - S dT, \quad (3.6)$$

suggesting that the convenient variables in which to express the Helmholtz free energy are the volume and the temperature. In the case of equilibrium, we find from Eq. (3.6) the important relations

$$\left(\frac{\partial A}{\partial V}\right)_T = -P, \quad \left(\frac{\partial A}{\partial T}\right)_V = -S. \quad (3.7)$$

The first of these shows that, at constant temperature, the Helmholtz free energy has some of the properties of a potential energy, in that its negative derivative with respect to a coordinate (the volume) gives the force (the pressure). If  $A$  is known as a function of  $V$  and  $T$ , the first Eq. (3.7) gives a relation between  $P$ ,  $V$ , and  $T$ , or the equation of state. From the second, we know entropy in terms of temperature and volume, and differentiating with respect to temperature at constant volume, using Eq. (2.4), we can find the specific heat. Thus a knowledge of the Helmholtz free energy as a function of volume and temperature gives both the equation of state and specific heat, or complete information about the system.

Instead of using volume and temperature as independent variables, however, we more often wish to use pressure and temperature. In this case, instead of using the Helmholtz free energy, it is more convenient to use the Gibbs free energy  $G$ , defined by the equations

$$G = H - TS = U + PV - TS = A + PV. \quad (3.8)$$

It will be seen that this function stands in the same relation to the enthalpy that the Helmholtz free energy does to the internal energy. We can now find the change of the Gibbs free energy  $G$  in any process. By definition, we have  $dG = dH - T dS - S dT$ . Using Eq. (3.2), this is  $dG = dU + P dV + V dP - T dS - S dT$ , and by Eq. (1) this is

$$dG \leq V dP - S dT. \quad (3.9)$$

For a system at constant pressure and temperature, we see that the Gibbs free energy is constant for a reversible process but decreases for an irreversible process, reaching a minimum value consistent with the pressure and temperature for the equilibrium state; just as for a system at constant volume the Helmholtz free energy is constant for a reversible process but decreases for an irreversible process. As with  $A$ , we can get the equation of state and specific heat from the derivatives of  $G$ , in equilibrium. We have

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \quad \left(\frac{\partial G}{\partial T}\right)_P = -S, \quad (3.10)$$

the first of these giving the volume as a function of pressure and temperature, the second the entropy as a function of pressure and temperature, from which we can find  $C_p$  by means of Eq. (2.6).

The Gibbs free energy  $G$  is particularly important on account of actual physical processes that occur at constant pressure and temperature. The most important of these processes is a change of phase, as the melting of a solid or the vaporization of a liquid. If unit mass of a substance changes phase reversibly at constant pressure and temperature, the total Gibbs free energy must be unchanged. That is, in equilibrium, the Gibbs free energy per unit mass must be the same for both phases. On the other hand, at a temperature and pressure which do not correspond to equilibrium between two phases, the Gibbs free energies per unit mass will be different for the two phases. Then the stable phase under these conditions must be that which has the lower Gibbs free energy. If the system is actually found in the phase of higher Gibbs free energy, it will be unstable and will irreversibly change to the other phase. Thus for instance, the Gibbs free energies of liquid and solid as functions of the temperature at atmospheric pressure are represented by curves which cross at the melting point. Below the melting point the solid has the lower Gibbs free energy. It is possible to have the liquid below the melting point; it is in the condition known as supercooling. But any slight disturbance is enough to produce a sudden and irreversible solidification, with reduction of Gibbs free energy, the final stable state being the solid. It is evident from these examples that the Gibbs free energy is of great importance in discussing physical and chemical processes. The Helmholtz free energy does not have any such importance. We shall see later, however, that the methods of statistical mechanics lead particularly simply to a calculation of the Helmholtz free energy, and its principal value comes about in this way.

**4. Methods of Deriving Thermodynamic Formulas.**—We have now introduced all the thermodynamic variables that we shall meet:  $P$ ,  $V$ ,  $T$ ,  $S$ ,  $U$ ,  $H$ ,  $A$ ,  $G$ . The number of partial derivatives which can be formed

from these is  $8 \times 7 \times 6 = 336$ , since each partial derivative involves one dependent and two independent variables, which must all be different. A few of these are familiar quantities, as we have seen in Sec. 2, but the great majority are unfamiliar. It can be shown,<sup>1</sup> however, that a relation can be found between any four of these derivatives, and certain of the thermodynamic variables. These relations are the thermodynamic formulas. Since there are 336 first derivatives, there are  $336 \times 335 \times 334 \times 333$  ways of picking out four of these, so that the number of independent relations is this number divided by  $4!$ , or 521,631,180 separate formulas. No other branch of physics is so rich in mathematical formulas, and some systematic method must be used to bring order into the situation. No one can be expected to derive any considerable number of the formulas or to keep them in mind. There are four principal methods of mathematical procedure used to derive these formulas, and in the present section we shall discuss them. Then in the next section we shall describe a systematic procedure for finding any particular formula that we may wish. The four mathematical methods of finding formulas are

1. We have already seen that there are a number of differential relations of the form

$$dx = K dy + L dz, \quad (4.1)$$

where  $K$  and  $L$  are functions of the variables. The most important relations of this sort which we have met are found in Eqs. (2.5), (3.2), (3.6), and (3.9), and are

$$\begin{aligned} dU &= -P dV + T dS, \\ dH &= V dP + T dS, \\ dA &= -P dV - S dT, \\ dG &= V dP - S dT. \end{aligned} \quad (4.2)$$

We have already seen in Eq. (2.6) how we can obtain formulas from such an expression. We can divide by the differential of one variable, say  $du$ , and indicate that the process is at constant value of another, say  $w$ . Thus we have

$$\left(\frac{\partial x}{\partial u}\right)_w = K \left(\frac{\partial y}{\partial u}\right)_w + L \left(\frac{\partial z}{\partial u}\right)_w. \quad (4.3)$$

In doing this, we must be sure that  $dx$  is the differential of a function of the state of the system, for only in that case is it proper to write a partial derivative like  $(\partial x/\partial u)_w$ . Thus in particular we cannot proceed in this way with expressions for  $dW$  and  $dQ$ , though superficially they look

<sup>1</sup> For the method of classifying thermodynamic formulas presented in Secs. 4 and 5, see P. W. Bridgman, "A Condensed Collection of Thermodynamic Formulas," Harvard University Press.

like Eq. (4.1). Using the method of Eq. (4.3), a very large number of formulas can be formed. A special case has been seen, for instance, in the Eqs. (2.7) and (2.8). This is the case in which  $u$  is one of the variables  $y$  or  $z$ , and  $w$  is the other. Thus, suppose  $u = y$ ,  $w = z$ . Then we have

$$\left(\frac{\partial x}{\partial y}\right)_z = K, \quad \text{and similarly} \quad \left(\frac{\partial x}{\partial z}\right)_y = L. \quad (4.4)$$

It is to be noted that, using Eq. (4.4), we may rewrite Eq. (4.1) in the form

$$\begin{aligned} dx &= K dy + L dz \\ &= \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz, \end{aligned} \quad (4.5)$$

a form in which it becomes simply the familiar mathematical equation expressing a total differential in terms of partial derivatives.

2. Suppose we have two derivatives such as  $(\partial x/\partial u)_z$ ,  $(\partial y/\partial u)_z$ , taken with respect to the same variable and with the same variable held constant. Since  $z$  is held fixed in both cases, they act like ordinary derivatives with respect to the variable  $u$ . But for ordinary derivatives we should have  $\frac{dx/du}{dy/du} = \frac{dx}{dy}$ . Thus, in this case we have

$$\frac{\left(\frac{\partial x}{\partial u}\right)_z}{\left(\frac{\partial y}{\partial u}\right)_z} = \left(\frac{\partial x}{\partial y}\right)_z. \quad (4.6)$$

We shall find that the relation in Eq. (4.6) is of great service in our systematic tabulation of formulas in the next section. For to find all partial derivatives holding a particular  $z$  constant, we need merely tabulate the six derivatives of the variables with respect to a particular  $u$ , holding this  $z$  constant. Then we can find any derivative of this type by Eq. (4.6).

3. Let us consider Eq. (4.5), and set  $x$  constant, or  $dx = 0$ . Then we may solve for  $dy/dz$ , and since  $x$  is constant, this will be  $(\partial y/\partial z)_x$ . Doing this, we have

$$\left(\frac{\partial y}{\partial z}\right)_x = -\frac{\left(\frac{\partial x}{\partial z}\right)_y}{\left(\frac{\partial x}{\partial y}\right)_z}. \quad (4.7)$$

Using Eq. (4.6), we can rewrite Eq. (4.7) in either of the two forms

$$\left(\frac{\partial y}{\partial z}\right)_x = -\frac{\left(\frac{\partial y}{\partial x}\right)_z}{\left(\frac{\partial z}{\partial x}\right)_y}, \quad (4.8)$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \quad (4.9)$$

The reader should note carefully the difference between Eq. (4.8) and Eq. (4.6). At first glance they resemble each other, except for the difference of sign; but it will be noted that in Eq. (4.6) each of the three derivatives has the same variable held constant, while in Eq. (4.8) each one has a different variable held constant.

4. We start with Eq. (4.4). Then we use the fundamental theorem regarding second partial derivatives:

$$\left[\frac{\partial}{\partial z}\left(\frac{\partial x}{\partial y}\right)_z\right]_y = \left[\frac{\partial}{\partial y}\left(\frac{\partial x}{\partial z}\right)_y\right]_z. \quad (4.10)$$

Substituting from Eq. (4.4), this gives us

$$\left(\frac{\partial K}{\partial z}\right)_y = \left(\frac{\partial L}{\partial y}\right)_z. \quad (4.11)$$

In Eq. (4.10), it is essential that  $x$  be a function of the state of the system, or of  $y$  and  $z$ . Four important relations result from applying Eq. (4.11) to the differential expressions (4.2). These are

$$\begin{aligned} -\left(\frac{\partial P}{\partial S}\right)_V &= \left(\frac{\partial T}{\partial V}\right)_S, \\ \left(\frac{\partial V}{\partial S}\right)_P &= \left(\frac{\partial T}{\partial P}\right)_S, \\ \left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T, \\ -\left(\frac{\partial V}{\partial T}\right)_P &= \left(\frac{\partial S}{\partial P}\right)_T. \end{aligned} \quad (4.12)$$

The Eqs. (4.12) are generally called Maxwell's relations.

We have now considered the four processes used in deriving thermodynamic formulas. By combinations of them, any desired relation connecting first derivatives can be obtained. In the next section we consider the classification of these formulas.

5. General Classification of Thermodynamic Formulas.—Bridgman<sup>1</sup> has suggested a very convenient method of classifying all the thermodynamic formulas involving first derivatives. As we have pointed out, a relation can be found between any four of the derivatives. Bridgman's method is then to write each derivative in terms of three standard derivatives, for which he chooses  $(\partial V/\partial T)_P$ ,  $(\partial V/\partial P)_T$ , and  $C_P = (\partial H/\partial T)_P$ . These are chosen because they can be found immediately from experiment, the first two being closely related to thermal expansion and compressibility [see Eqs. (2.1) and (2.2)]. If now we wish a relation between two derivatives, we can write each in terms of these standard derivatives, and the relations will immediately become plain. Our task, then, is to find all but these three of the 336 first partial derivatives, in terms of these three. As a matter of fact, we do not have to tabulate nearly all of these, on account of the usefulness of Eq. (4.6). We shall tabulate all derivatives of the form  $(\partial x/\partial T)_P$ ,  $(\partial x/\partial P)_T$ ,  $(\partial x/\partial T)_V$ , and  $(\partial x/\partial T)_S$ . Then by application of Eq. (4.6), we can at once find any derivative whatever at constant  $P$ , constant  $T$ , constant  $V$ , or constant  $S$ . We could continue the same thing for finding derivatives holding the other quantities fixed; but we shall not need such derivatives very often, and they are very easily found by application of methods (2) and (3) of the preceding section, and by the use of our table. We shall now tabulate these derivatives, later indicating the derivations of the only ones that are at all involved, and giving examples of their application. We shall be slightly more general than Bridgman, in that alternative forms are given for some of the equations in terms either of  $C_P$  or  $C_V$ .

TABLE I-1.—TABLE OF THERMODYNAMIC RELATIONS

$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_P &= \left(\frac{\partial V}{\partial T}\right)_P \\ \left(\frac{\partial S}{\partial T}\right)_P &= \frac{C_P}{T} \\ \left(\frac{\partial U}{\partial T}\right)_P &= C_P - P\left(\frac{\partial V}{\partial T}\right)_P \\ \left(\frac{\partial H}{\partial T}\right)_P &= C_P \\ \left(\frac{\partial A}{\partial T}\right)_P &= -P\left(\frac{\partial V}{\partial T}\right)_P - S \\ \left(\frac{\partial G}{\partial T}\right)_P &= -S \end{aligned}$$

<sup>1</sup> See reference under Sec. 4.

TABLE I-1.—TABLE OF THERMODYNAMIC RELATIONS (Continued)

$$\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial A}{\partial P}\right)_T = -P\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} = \frac{C_P}{T} + \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = C_P + T\frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\left(\frac{\partial H}{\partial T}\right)_V = C_V - V\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = C_P + T\frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} - V\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial G}{\partial T}\right)_V = -S - V\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}$$

TABLE I-1.—TABLE OF THERMODYNAMIC RELATIONS (Continued)

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{T\left(\frac{\partial V}{\partial T}\right)_P}$$

$$\left(\frac{\partial V}{\partial T}\right)_S = \frac{\left(\frac{\partial V}{\partial P}\right)_T C_V}{\left(\frac{\partial V}{\partial T}\right)_P T} = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P} \left[ \frac{C_P}{T} + \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \right]$$

$$\left(\frac{\partial U}{\partial T}\right)_S = -P\frac{\left(\frac{\partial V}{\partial P}\right)_T C_V}{\left(\frac{\partial V}{\partial T}\right)_P T} = -P\frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P} \left[ \frac{C_P}{T} + \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \right]$$

$$\left(\frac{\partial H}{\partial T}\right)_S = \frac{VC_P}{T\left(\frac{\partial V}{\partial T}\right)_P}$$

$$\left(\frac{\partial A}{\partial T}\right)_S = -P\frac{\left(\frac{\partial V}{\partial P}\right)_T C_V}{\left(\frac{\partial V}{\partial T}\right)_P T} - S$$

$$= -P\frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P} \left[ \frac{C_P}{T} + \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \right] - S$$

$$\left(\frac{\partial G}{\partial T}\right)_S = \frac{VC_P}{T\left(\frac{\partial V}{\partial T}\right)_P} - S$$

The formulas of Table I-1 all follow in very obvious ways from the methods of Sec. 4, except perhaps the relation between  $C_V$  and  $C_P$ , used in the derivatives at constant  $V$  and constant  $S$ . To prove the relation between these two specific heats, we proceed as follows. We have

$$\begin{aligned} T dS &= T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \\ &= T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP. \end{aligned} \quad (5.1)$$

We subtract the first of Eqs. (5.1) from the second, and set  $dV = 0$ , obtaining

$$(C_P - C_V)dT = T\left(\frac{\partial V}{\partial T}\right)_P dP.$$

Dividing by  $dT$ , this is

$$(C_p - C_v) = T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_V = -T \frac{\left( \frac{\partial V}{\partial T} \right)_P^2}{\left( \frac{\partial V}{\partial P} \right)_T} \quad (5.2)$$

the result used in the formulas of Table I-1. The result of Eq. (5.2) is an important formula, and is the generalization holding for all substances of the familiar formula  $C_p - C_v = nR$  holding for perfect gases. It serves in any case to find  $C_p - C_v$  from the equation of state. Since  $(\partial V/\partial P)_T$  is always negative, we see that  $C_p$  is always greater than  $C_v$ .

#### 6. Comparison of Thermodynamic and Gas Scales of Temperature.—

In Chap. I, Sec. 4, we have discussed the thermodynamic temperature, introduced in the statement of the second law of thermodynamics, and we have mentioned that it can be proved that this is the same temperature that is measured by a gas thermometer. We are now in position to prove this fact. First, we must define a perfect gas in a way that could be applied experimentally without knowing any temperature scale except that furnished by the gas itself. We can define it as a gas which in the first place obeys Boyle's law:  $PV = \text{constant}$  at constant temperature, or  $PV = f(T)$ , where  $T$  is the thermodynamic temperature, and  $f$  is a function as yet unknown. Secondly, it obeys what is called Joule's law: the internal energy  $U$  is independent of the volume at constant temperature. These assumptions can both be proved by direct experiment. We can certainly observe constancy of temperature without a temperature scale, so that we can verify Boyle's law. To check Joule's law, we may consider the free expansion of the gas. We let the gas expand irreversibly into a vacuum. It is assumed that the process is carried out adiabatically, and since there is no external work done, the internal energy is unchanged in the process. We allow the gas to come to equilibrium at its new volume, and observe whether the temperature is the same that it was originally, or different. If it is the same, then the gas is said to obey Joule's law. To check the mathematical formulation of this law, we note that the experiment of free expansion tells us directly that the temperature is independent of volume, at constant internal energy:  $(\partial T/\partial V)_U = 0$ . But by Eq. (4.9), we have

$$\left( \frac{\partial U}{\partial V} \right)_T = - \left( \frac{\partial U}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_U = -C_v \left( \frac{\partial T}{\partial V} \right)_U = 0. \quad (6.1)$$

Equation (6.1) states that the internal energy is independent of volume at constant temperature, the usual statement of Joule's law.

Without further assumption about the gas, we can now prove that  $f(T) = \text{constant} \times T$ , so that the pressure of a perfect gas at constant

volume is proportional to the thermodynamic temperature, and if we use proper units, the gas scale of temperature is identical with the thermodynamic scale. Using Table I-1 we have the important general relation

$$\left( \frac{\partial U}{\partial V} \right)_T = -T \frac{\left( \frac{\partial V}{\partial T} \right)_P}{\left( \frac{\partial V}{\partial P} \right)_T} - P = T \left( \frac{\partial P}{\partial T} \right)_V - P, \quad (6.2)$$

giving the change of internal energy with volume of any substance at constant temperature. We set this equal to zero, on account of Joule's law. From the equation of state,

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{f'(T)}{V} = P \frac{f'(T)}{f(T)}. \quad (6.3)$$

Substituting Eq. (6.3) in Eq. (6.2), and canceling out a factor  $P$ , we have

$$T \frac{f'(T)}{f(T)} = 1,$$

or

$$d \ln f = d \ln T, \quad \ln f(T) = \ln T + \text{const.}, \\ f(T) = \text{const.} \times T, \quad (6.4)$$

which was to be proved.

Instead of defining a perfect gas as we have done, by Boyle's law and Joule's law, we may prefer to assume that a thermodynamic temperature scale is known, and that the perfect gas satisfies the general gas law  $PV = \text{const.} \times T$ . Then we can at once use the relation (6.2) to calculate the change of internal energy with volume at constant temperature, and find it to be zero. That is, we show directly by thermodynamics that Joule's law follows from the gas law, if that is stated in terms of the thermodynamic temperature.



### CHAPTER III STATISTICAL MECHANICS

Thermodynamics is a simple, general, logical science, based on two postulates, the first and second laws of thermodynamics. We have seen in the last chapter how to derive results from these laws, though we have not used them yet in our applications. But we have seen that they are limited. Typical results are like Eq. (5.2) in Chap. II, giving the difference of specific heats of any substance,  $C_p - C_v$ , in terms of derivatives which can be found from the equation of state. Thermodynamics can give relations, but it cannot derive the specific heat or equation of state directly. To do that, we must go to the statistical or kinetic methods. Even the second law is simply a postulate, verified because it leads to correct results, but not derived from simpler mechanical principles as far as thermodynamics is concerned. We shall now take up the statistical method, showing how it can lead not only to the equation of state and specific heat, but to an understanding of the second law as well.

1. Statistical Assemblies and the Entropy.—To apply statistics to any problem, we must have a great many individuals whose average properties we are interested in. We may ask, what are the individuals to which we apply statistics, in statistical mechanics? The answer is, they are a great many repetitions of the same experiment, or replicas of the same system, identical as far as all large-scale, or macroscopic, properties are concerned, but differing in the small-scale, or microscopic, properties which we cannot directly observe. A collection of such replicas of the same system is called a statistical assembly (or, following Gibbs, an ensemble). Our guiding principle in setting up an assembly is to arrange it so that the fluctuation of microscopic properties from one system to another of the assembly agrees with the amount of such fluctuation which would actually occur from one repetition to another of the same experiment.

Let us ask what the randomness that we associated with entropy in Chap. I means in terms of the assembly. A random system, or one of large entropy, is one in which the microscopic properties may be arranged in a great many different ways, all consistent with the same large-scale behavior. Many different assignments of velocity to individual molecules, for instance, can be consistent with the picture of a gas at high temperatures, while in contrast the assignment of velocity to molecules at the absolute zero is definitely fixed: all the molecules are at rest. Then

to represent a random state we must have an assembly which is distributed over many microscopic states, the randomness being measured by the wideness of the distribution. We can make this idea more precise. Following Planck, we may refer to a particular microscopic state of the system as a complexion. We may describe an assembly by stating what fraction of the systems of the assembly is found in each possible complexion. We shall call this fraction, for the  $i$ th complexion,  $f_i$ , and shall refer to the set of  $f_i$ 's as the distribution function describing the assembly. Plainly, since all systems must be in one complexion or another,

$$\sum_i f_i = 1. \quad (1.1)$$

Then in a random assembly, describing a system of large entropy, there will be systems of the assembly distributed over a great many complexions, so that many  $f_i$ 's will be different from zero, each one of these fractions being necessarily small. On the other hand, in an assembly of low entropy, systems will be distributed over only a small number of complexions, so that only a few  $f_i$ 's will be different from zero, and these will be comparatively large.

We shall now postulate a mathematical definition of entropy, in terms of the  $f_i$ 's, which is large in the case of a random distribution, small otherwise. This definition is

$$S = -k \sum_i f_i \ln f_i. \quad (1.2)$$

Here  $k$  is a constant, called Boltzmann's constant, which will appear frequently in our statistical work. It has the same dimensions as entropy, or specific heat, that is, energy divided by temperature. Its value in absolute units is  $1.379 \times 10^{-16}$  erg per degree. This value is derived indirectly; using Eq. (1.2), for the entropy, one can derive the perfect gas law and the gas constant, in terms of  $k$ , thereby determining  $k$  from experiment.

It is easy to see that Eq. (1.2) has the required property of being large for a randomly arranged system, small for one with no randomness. If there is no randomness at all, all values of  $f_i$  will be zero, except one, which will be unity. But the function  $f \ln f$  is zero when  $f$  is either zero or unity, so that the entropy in this case will be zero, its lowest possible value. On the other hand, if the system is a random one, many complexions will have  $f_i$  different from zero, equal to small fractions, so that their logarithms will be large negative quantities, and the entropy will be large and positive. We can see this more clearly if we take a simple case: suppose the assembly is distributed through  $W$  complexions, with

equal fractions in each. The value of each  $f_i$  in these complexions is  $1/W$ , while for other complexions  $f_i$  is zero. Then we have

$$\begin{aligned} S &= -kW \frac{1}{W} \ln \frac{1}{W} \\ &= k \ln W. \end{aligned} \quad (1.3)$$

The entropy, in such a case, is proportional to the logarithm of the number of complexions in which systems of the assembly can be found. As this number of complexions increases, the distribution becomes more random or diffuse, and the entropy increases.

Boltzmann<sup>1</sup> based his theory of the relation of probability to entropy on Eq. (1.3), rather than using the more general relation (1.2). He called  $W$  the thermodynamic probability of a state, arguing much as we have that a random state, which is inherently likely to be realized, will have a large value of  $W$ . Planck<sup>2</sup> has shown by the following simple argument that the logarithmic form of Eq. (1.3) is reasonable. Suppose the system consists of two parts, as for instance two different masses of gas, not connected with each other. In a given state, represented by a given assembly, let there be  $W_1$  complexions of the first part of the system consistent with the macroscopic description of the state, and  $W_2$  complexions of the second part. Then, since the two parts of the system are independent of each other, there must be  $W_1W_2$  complexions of the combined system, since each complexion of the first part can be joined to any one of the complexions of the second part to give a complexion of the combined system. We shall then find for the entropy of the combined system

$$\begin{aligned} S &= k \ln W_1W_2 \\ &= k \ln W_1 + k \ln W_2. \end{aligned} \quad (1.4)$$

But if we considered the first part of the system by itself, it would have an entropy  $S_1 = k \ln W_1$ , and the second part by itself would have an entropy  $S_2 = k \ln W_2$ . Thus, on account of the relation (1.3), we have

$$S = S_1 + S_2. \quad (1.5)$$

But surely this relation must be true; in thermodynamics, the entropy of two separated systems is the sum of the entropies of the parts, as we can see directly from the second law, since the changes of entropy,  $dQ/T$ , in a reversible process, are additive. Then we can reverse the argument above. Equation (1.5) must be true, and if the entropy is a function of  $W$ , it can be shown that the only possible function consistent with the additivity of the entropy is the logarithmic function of Eq. (1.3).

<sup>1</sup> See for example, L. Boltzmann, "Vorlesungen über Gastheorie," Sec. 6, J. A. Barth.

<sup>2</sup> See for example, M. Planck, "Heat Radiation," Sec. 119, P. Blakiston's Sons & Company.

Going back to our more general formula (1.2), we can show that if the assembly is distributed through  $W$  complexions, the entropy will have its maximum value when the  $f_i$ 's are of equal magnitude, and is reduced by any fluctuation in  $f_i$  from cell to cell, verifying that any concentration of systems in particular complexions reduces the entropy. Taking the formula (1.2) for entropy, we find how it changes when the  $f_i$ 's are varied. Differentiating, we have at once

$$dS = -k \sum_i (1 + \ln f_i) df_i. \quad (1.6)$$

But we know from Eq. (1.1) that  $\sum_i f_i = 1$ , from which at once

$$\sum_i df_i = 0. \quad (1.7)$$

Thus the first term of Eq. (1.6) vanishes; and if we assume that the density is uniform, so that  $\ln f_i$  is really independent of  $f_i$ , we can take it out of the summation in Eq. (1.6) as a common factor, and the remaining term will vanish too, giving  $dS = 0$ . That is, for uniform density, the variation of the entropy for small variations of the assembly vanishes, a necessary condition for a maximum of the entropy. A little further investigation would convince us that this really gives a maximum, not a minimum, of entropy, and that in fact Eq. (1.3) gives the absolute maximum, the highest value of which  $S$  is capable, so long as only  $W$  complexions are represented in the assembly. The only way to get a still greater value of  $S$  would be to have more terms in the summation, so that each individual  $f_i$  could be even less.

We have postulated a formula for the entropy. How can we expect to prove that it is correct? We can do this only by going back to the second law of thermodynamics, showing that our entropy has the properties demanded by that law, and that in terms of it the law is satisfied. We have already shown that our formula for the entropy has one of the properties demanded of the entropy: it is determined by the state of the system. In statistical mechanics, the only thing we can mean by the state of the system is the statistical assembly, since this determines average or observable properties of all sorts, and our formula (1.2) for entropy is determined by the statistical assembly. Next we must show that our formula represents a quantity that increases in an irreversible process. This will be done by qualitative but valid reasoning in a later section. It will then remain to consider thermal equilibrium and reversible processes, and to show that in such processes the change of entropy is  $dQ/T$ .

2. Complexions and the Phase Space.—We wish to find how our formula for the entropy changes in an irreversible process. To do this, we must find how the  $f_i$ 's change with time, or how systems of the assembly, as time goes on, change from one complexion to another. This is a problem in kinetics, and we shall not take it up quantitatively until the chapter on kinetic methods. For the present we shall be content with qualitative discussions. The first thing that we must do is to get a more precise definition of a complexion. We have a certain amount of information to guide us in making this definition. We are trying to make our definition of entropy agree with experience, and in particular we want the state of maximum entropy to be the stable, equilibrium state. But we have just seen that for an assembly distributed through  $W$  complexions, the state of maximum entropy is that in which equal numbers of systems are found in each complexion. This is commonly expressed by saying that complexions have equal a priori probability; that is, if we have no specific information to the contrary, we are as likely to find a system of an assembly in one complexion as in another, in equilibrium. Our definition of a complexion, then, must be consistent with this situation.

The method of defining complexions depends on whether we are treating our systems by classical, Newtonian mechanics or by quantum theory. First we shall take up classical mechanics, for that is more familiar. But later, when we describe the methods of quantum theory, we shall observe that that theory is more correct and more fundamental for statistical purposes. In classical mechanics, a system is described by giving the coordinates and velocities of all its particles. Instead of the velocities, it proves to be more desirable to use the momenta. With rectangular coordinates, the momentum associated with each coordinate is simply the mass of the particle times the corresponding component of velocity; with angular coordinates a momentum is an angular momentum; and so on. If there are  $N$  coordinates and  $N$  momenta (as for instance the rectangular coordinates of  $N/3$  particles, with their momenta), we can then visualize the situation by setting up a  $2N$  dimensional space, called a phase space, in which the coordinates and momenta are plotted as variables, and a single point, called a representative point, gives complete information about the system. An assembly of systems corresponds to a collection of representative points, and we shall generally assume that there are so many systems in the assembly that the distribution of representative points is practically continuous in the phase space. Now a complexion, or microscopic state, of the system must correspond to a particular point, or small region, of the phase space; to be more precise, it should correspond to a small volume of the phase space. We subdivide the whole phase space into small volume elements and call each volume element a complexion, saying that  $f_i$ , the fraction of systems of the assembly in a

particular complexion, simply equals the fraction of all representative points in the corresponding volume element. The only question that arises, then, is the shape and size of volume elements representing complexions.

To answer this question, we must consider how points move in the phase space. We must know the time rates of change of all coordinates and momenta, in terms of the coordinates and momenta themselves. Newton's second law gives us the time rate of change of each momentum, stating that it equals the corresponding component of force, which is a function of the coordinates in a conservative system. The time rate of change of each coordinate is simply the corresponding velocity component, which can be found at once from the momentum. Thus we can find what is essentially the  $2N$  dimensional velocity vector of each representative point. This velocity vector is determined at each point of phase space and defines a rate of flow, the representative points streaming through the phase space as a fluid would stream through ordinary space. We are thus in a position to find how many points enter or leave each element of volume, or each complexion, per unit time, and therefore to find the rate at which the fraction of systems in that complexion changes with time. It is now easy to prove, from the equations of motion, a general theorem called Liouville's theorem.<sup>1</sup> This theorem states, in mathematical language, the following fact: the swarm of points moves in such a way that the density of points, as we follow along with the swarm, never changes. The flow is like a streamline flow of an incompressible fluid, each particle of fluid always preserving its own density. This does not mean that the density at a given point of space does not change with time; in general it does, for in the course of the flow, first a dense part of the swarm, then a less dense one, may well be swept by the point in question, as if we had an incompressible fluid, but one whose density changed from point to point. It does mean, however, that we can find a very simple condition which is necessary and sufficient for the density at a given point of space to be independent of time: the density of points must be constant all along each streamline, or tube of flow, of the points. For then, no matter how long the flow continues, the portions of the swarm successively brought up to the point in question all have the same density, so that the density there can never change.

To find the condition for equilibrium, then, we must investigate the nature of the streamlines. For a periodic motion, a streamline will be closed, the system returning to its original state after a single period. This is a very special case, however; most motions of many particles are not periodic and their streamlines never close. Rather, they wind around

<sup>1</sup>For proof, see for example, Slater and Frank, "Introduction to Theoretical Physics," pp. 365-366, McGraw-Hill Book Company, Inc., 1933.

in a very complicated way, coming in the course of time arbitrarily close to every point of phase space corresponding to the same total energy (of course the energy cannot change with time, so that the representative point must stay in a region of constant energy in the phase space). Such a motion is called quasi-ergodic, and it can be shown to be the general type of motion, periodic motions being a rare exception. Then, from the statement in the last paragraph, we see that to have a distribution independent of time, we must have a density of points in phase space which is constant for all regions of the same energy. But on the other hand thermal equilibrium must correspond to a distribution independent of time, and we have seen that the state of maximum entropy is one in which all complexions have the same number of systems. These two statements are only compatible if each complexion corresponds to the same volume of phase space. For then a constant volume density of points, which by Liouville's theorem corresponds to a distribution independent of time, will at the same time correspond to a maximum entropy. We thus draw the important conclusion that regions of equal volume in phase space have equal a priori probability, or that a complexion corresponds to a quite definite volume of phase space. Classical mechanics, however, does not lead to any way of saying how large this volume is. Thus it cannot lead to any unique definition of the entropy; for the  $f_i$ 's depend on how large a volume each complexion corresponds to, and they in turn determine the entropy.

**3. Cells in the Phase Space and the Quantum Theory.**—Quantum mechanics starts out quite differently from classical mechanics. It does not undertake to say how the coordinates and momenta of the particles change as time goes on. Rather, it is a statistical theory from the beginning: it sets up a statistical assembly, and tells us directly how that assembly changes with time, without the intermediate step of solving for the motion of individual systems by Newton's laws of motion. And it describes the assembly, from the outset, in terms of definite complexions, so that the problem of defining the complexions is answered as one of the postulates of the theory. It sets up quantum states, of equal a priori probability, and describes an assembly by giving the fraction of all systems in each quantum state. Instead of giving laws of motion, like Newton's second law, its fundamental equation is one telling how many systems enter or leave each quantum state per second. In particular, if equal fractions of the systems are found in all quantum states associated with the same energy, we learn that these fractions will not change with time; that is, in a steady or equilibrium state all the quantum states are equally occupied, or have equal a priori probabilities. We are then entirely justified in identifying these quantum states with the complexions which we have mentioned. When we deal with quantum statistics,

$f_i$  will refer to the fraction of all systems in the  $i$ th quantum state. This gives a definite meaning to the complexions, and leads to a definite numerical value for the entropy.

Quantum theory provides no unique way of setting up the quantum states, or the complexions. We can understand this much better by considering the phase space. Many features of the quantum theory can be described by dividing the phase space into cells of equal volume, and associating each cell with a quantum state. The volume of these cells is uniquely fixed by the quantum theory, but not their shape. We can, for example, take simply rectangular cells, of dimensions  $\Delta q_1$  along the axis representing the first coordinate,  $\Delta q_2$  for the second coordinate, and so on up to  $\Delta q_N$  for the  $N$ th coordinate, and  $\Delta p_1$  to  $\Delta p_N$  for the corresponding momenta. Then there is a very simple rule giving the volume of such a cell: we have

$$\Delta q_i \Delta p_i = h, \quad (3.1)$$

where  $h$  is Planck's constant, equal numerically to  $6.61 \times 10^{-27}$  absolute units. Thus, with  $N$  coordinates, the  $2N$ -dimensional volume of a cell is  $h^N$ .

We can equally well take other shapes of cells. A method which is often useful can be illustrated with a problem having but one coordinate  $q$  and one momentum  $p$ . Then in our two-dimensional phase space we can draw a curve of constant energy. Thus for instance consider a particle of mass  $m$  held to a position of equilibrium by a restoring force proportional to the displacement, so that its energy is

$$E = \frac{p^2}{2m} + 2\pi^2 m \nu^2 q^2, \quad (3.2)$$

where  $\nu$  is the frequency with which it would oscillate in classical mechanics. The curves of constant energy are then ellipses in the  $p$ - $q$  space, as we see by writing the equation in the form

$$\frac{p^2}{(\sqrt{2mE})^2} + \frac{q^2}{(\sqrt{E/2\pi^2 m \nu^2})^2} = 1, \quad (3.3)$$

the standard form for the equation of an ellipse of semiaxes  $\sqrt{2mE}$  and  $\sqrt{E/2\pi^2 m \nu^2}$ . Such an ellipse is shown in Fig. III-1. Then we can choose cells bounded by such curves of constant energy, such as those indicated in Fig. III-1. Since the area between curves must be  $h$ , it is plain that the  $n$ th ellipse must have an area  $nh$ , where  $n$  is an integer. The area of an ellipse of semiaxes  $a$  and  $b$  is  $\pi ab$ ; thus in this case we have an area of  $\pi \sqrt{2mE} \sqrt{E/2\pi^2 m \nu^2} = E/\nu$ , so that the energy of the ellipse connected

with a given integer  $n$  is given by

$$E_n = nh\nu. \quad (3.4)$$

Another illustration of this method is provided by a freely rotating wheel of moment of inertia  $I$ . The natural coordinate to use to describe it is the angle  $\theta$ , and the corresponding momentum  $p_\theta$  is the angular momen-

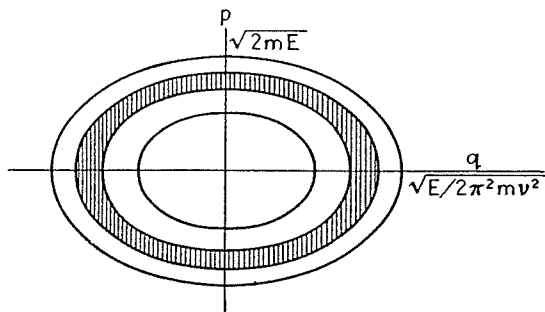


FIG. III-1.—Cells in phase space, for the linear oscillator. The shaded area, between two ellipses of constant energy, has an area  $h$  in the quantum theory.

tum,  $I\omega$ , where  $\omega = d\theta/dt$  is the angular velocity. If no torques act, the energy is wholly kinetic, equal to

$$E = \frac{1}{2}I\omega^2 = p_\theta^2/2I. \quad (3.5)$$

Then, as shown in Fig. III-2, lines of constant energy are straight lines at constant value of  $p_\theta$ . Since  $\theta$  goes from zero to  $2\pi$ , and then the motion repeats, we use only values of the coordinate in this range. Then, if the cells are set up so that the area of each is  $h$ , we must have them bounded by the lines

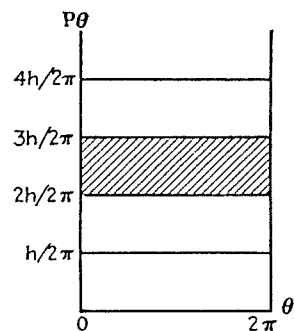


FIG. III-2.—Cells in phase space, for the rotator. The shaded area has an area of  $h$  in the quantum theory.

in terms of these cells, we can now understand one of the most fundamental statements of the quantum theory, the principle of uncertainty: it is impossible to regulate the coordinates and momenta of a system more accurately than to require that they lie somewhere within a given cell. Any attempt to be more precise, on account of the necessary clumsiness of nature, will result in a disturbance of the system just great enough to

$$p_\theta = \frac{nh}{2\pi}, \quad (3.6)$$

so that the energy associated with the  $n$ th line is

$$E_n = \frac{n^2h^2}{8\pi^2I}. \quad (3.7)$$

shift the representative points in an unpredictable way from one part of the cell to another. The best we can do in setting up an assembly, in other words, is to specify what fraction of the systems will be found in each quantum state or complexion, or to give the  $f_i$ 's. This does not imply by any means, however, that it does not make sense to talk about the coordinates and momenta of particles with more accuracy than to locate the representative point in a given cell. There is nothing inherently impossible in knowing the coordinates and momenta of a system as accurately as we please; the restriction is only that we cannot prepare a system, or an assembly of systems, with as precisely determined coordinates and momenta as we might please.

Since we may be interested in precise values of the momenta and coordinates of a system, there must be something in the mathematical framework of the theory to describe them. We must be able to answer questions of this sort: given, that an assembly has a given fraction of its systems in each cell of phase space, what is the probability that a certain quantity, such as one of the coordinates, lies within a certain infinitesimal range of values? Put in another way, if we know that a system is in a given cell, what is the probability that its coordinates and momenta lie in definite ranges? The quantum theory, and specifically the wave mechanics, can answer such questions; and because it can, we are justified in regarding it as an essentially statistical theory. By experimental methods, we can insure that a system lies in a given cell of phase space. That is, we can prepare an assembly all of whose representative points lie in this single cell, but this is the nearest we can come to setting up a system of quite definite coordinates and momenta. Having prepared such an assembly, however, quantum theory says that the coordinates and momenta will be distributed in phase space in a definite way, quite independent of the way we prepared the assembly, and therefore quite unpredictable from the previous history of the system. In other words, all that the theory can do is to give us statistical information about a system, not detailed knowledge of exactly what it will do. This is in striking contrast to the classical mechanics, which allows precise prediction of the future of a system if we know its past history.

The cells of the type described in Figs. III-1 and III-2 have a special property: all the systems in such a quantum state have the same energy. The momenta and coordinates vary from system to system, roughly as if systems were distributed uniformly through the cell, as for example through the shaded area of either figure, though as a matter of fact the real distribution is much more complicated than this. But the energy is fixed, the same for all systems, and is referred to as an energy level. It is equal to some intermediate energy value within the cell in phase space, as computed classically. Thus for the oscillator, as a matter of fact, the

energy levels are

$$E_n = \left(n + \frac{1}{2}\right)h\nu, \quad (3.8)$$

which, as we see from Eq. (3.4), is the energy value in the middle of the cell, and for a rotator the energy value is

$$E_n = n(n + 1) \frac{h^2}{8\pi^2 I}, \quad (3.9)$$

approximately the mean value through the cell. The integer  $n$  is called the quantum number. The distribution of points in a quantum state of fixed energy is independent of time, and for that reason the state is called a stationary state. This is in contrast to other ways of setting up cells. For instance, with rectangular cells, we find in general that the systems in one state have a distribution of energies, and as time goes on systems jump at a certain rate from one state to another, having what are called quantum transitions, so that the number of systems in each state changes with time. One can draw a certain parallel, or correspondence, between the jumping of systems from one quantum state to another, and the uniform flow of representative points in the phase space in classical mechanics. Suppose we have a classical assembly whose density in the phase space changes very slowly from point to point, changing by only a small amount in going from what would be one quantum cell to another. Then we can set up a quantum assembly, the fraction of systems in each quantum state being given by the fraction of the classical systems in the corresponding cell of phase space. And the time rate of change of the fraction of systems in each quantum state will be given, to a good approximation, by the corresponding classical value. This correspondence breaks down, however, as soon as the density of the classical assembly changes greatly from cell to cell. In that case, if we set up a quantum assembly as before, we shall find that its time variation does not agree at all accurately with what we should get by use of our classical analogy.

Actual atomic systems obey the quantum theory, not classical mechanics, so that we shall be concerned with quantum statistics. The only cases in which we can use classical theory as an approximation are those in which the density in phase varies only a little from state to state, —the case we have mentioned in the last paragraph. As a matter of fact, as we shall see later, this corresponds roughly to the limit of high temperature. Thus, we shall often find that classical results are correct at high temperatures but break down at low temperature. A typical example of this is the theory of specific heat; we shall find others as we go on. We now understand the qualitative features of quantum statistics well enough so that in the next section we can go on to our task of understanding the

nature of irreversible processes and the way in which the entropy increases with time in such processes.

**4. Irreversible Processes.**—We shall start our discussion of irreversible processes using classical mechanics and Liouville's theorem. Let us try to form a picture of what happens when we start with a system out of equilibrium, with constant energy and volume, follow its irreversible change into equilibrium, and examine its final steady state. To have a specific example, consider the approach to equilibrium of a perfect gas having a distribution of velocities which originally does not correspond to thermal equilibrium. Assume that at the start of an experiment, a mass of gas is rushing in one direction with a large velocity, as if it had just been shot into a container from a jet. This is far from an equilibrium distribution. The random kinetic energy of the molecules, which we should interpret as heat motion, may be very small and the temperature low, and yet they have a lot of kinetic energy on account of their motion in the jet. In the phase space, the density function will be large only in the very restricted region where all molecules have almost the same velocity, the velocity of the jet (that is, the equations

$$\frac{p_{x1}}{m_1} = \frac{p_{x2}}{m_2} = \dots = V_x, \text{ etc.,}$$

where  $V_x$  is the  $x$  component of velocity of the jet, are almost satisfied by all points in the assembly), and all have coordinates near the coordinate of the center of gravity of the rushing mass of gas (that is, the equations  $x_1 = x_2 = \dots = X$ , where  $X$  is the  $x$  coordinate of the center of gravity of the gas, are also approximately satisfied). We see, then, that the entropy, as defined by  $-k \sum_i f_i \ln f_i$ , will be small under these conditions.

But as time goes on, the distribution will change. The jet of molecules will strike the opposite wall of the container, and after bouncing back and forth a few times, will become more and more dissipated, with irregular currents and turbulence setting in. At first we shall describe these things by hydrodynamics or aerodynamics, but we shall find that the description of the flow gets more and more complicated with irregularities on a smaller and smaller scale. Finally, with the molecules colliding with the walls and with each other, things will become extremely involved, some molecules being slowed down, some speeded up, the directions changed, so that instead of having most of the molecules moving with almost the same velocity and located at almost the same point of space, there will be a whole distribution of momentum, both in direction and magnitude, and the mass will cease its concentration in space and will be uniformly distributed over the container. There will now be a great

many points of phase space representing states of the system which could equally well be this final state, so that the entropy will be large. And the increase of entropy has come about at the stage of the process where we cease to regard the complication in the motion as large-scale turbulence, and begin to classify it as randomness on a microscopic or atomic scale. Finally the gas will come to an equilibrium state, in which it no longer changes appreciably with time, and in this state it will have reached its maximum entropy consistent with its total energy.

This qualitative argument shows what we understand by an irreversible process and an increase of entropy: an assembly, originally concentrated in phase space, changes on account of the motion of the system in such a way that the points of the assembly gradually move apart, filling up larger and larger regions of phase space. This is likely, for there are many ways in which it can happen; while the reverse process, a concentration of points, is very unlikely, and we can for practical purposes say that it does not happen.

The statement we have just made seems at first to be directly contrary to Liouville's theorem, for we have just said that points originally concentrated become dispersed, while Liouville's theorem states that as we follow along with a point, the density never changes at all. We can give an example used by Gibbs<sup>1</sup> in discussing this point. Suppose we have a bottle of fluid consisting of two different liquids, one black and one white, which do not mix with each other. We start with one black drop in the midst of the white liquid, corresponding to our concentrated assembly. Now we shake or stir the liquid. The black drop will become shaken into smaller drops, or be drawn out into thin filaments, which will become dispersed through the white liquid, finally forming something like an emulsion. Each microscopic black drop or filament is as black as ever, corresponding to the fact that the density of points cannot change in the assembly. But eventually the drops will become small enough and uniformly enough dispersed so that each volume element within the bottle will seem uniformly gray. This is something like what happens in the irreversible mixing of the points of an assembly. Just as a droplet of black fluid can break up into two smaller droplets, its parts traveling in different directions, so it can happen that two systems represented by adjacent representative points can separate and have quite different histories; one may be in position for certain molecules to collide, while the other may be just different enough so that these molecules do not collide at all, for example. Such chance events will result in very different detailed histories for the various systems of an assembly, even if the original systems of the assembly were quite similar. That is, they will

<sup>1</sup>J. W. Gibbs, "Elementary Principles in Statistical Mechanics," Chap. XII, Longmans, Green & Company.

result in representative points which were originally close together in phase space moving far apart from each other.

From the example and the analogy we have used, we see that in an irreversible process the points of the original compact and orderly assembly gradually get dissipated and mixed up, with consequent increase of entropy. Now let us see how the situation is affected when we consider the quantum theory and the finite size of cells in phase space. Our description of the process will depend a good deal on the scale of the mixing involved in the irreversible process. So long as the mixing is on a large scale, by Liouville's theorem, the points that originally were in one cell will simply be moved bodily to another cell, so that the contribution of these points to  $-k\Sigma f_i \ln f_i$  will be the same as in the original distribution, and the entropy will be unchanged. The situation is very different, however, when the distribution as we should describe it by classical mechanics involves a set of filaments, of different densities, on a scale small compared to a cell. Then the quantum  $f_i$ , rather than equaling the classical value, will be more nearly the average of the classical values through the cell, leading to an increase of entropy, at the same time that the average or quantum density begins to disobey Liouville's theorem.

It is at this same stage of the process that it becomes really impossible to reverse the motion. It is a well-known result of Newton's laws that if, at a given instant, all the positions of all particles are left unchanged, but all velocities are reversed in direction, the whole motion will reverse, and go back over its past history. Thus every motion is, in theory, reversible. What is it that in practice makes some motions reversible, others irreversible? It is simply the practicability of setting up the system with reversed velocities. If the distribution of velocities is on a scale large enough to see and work with, there is nothing making a reversal of the velocities particularly hard to set up. With our gas, we could suddenly interpose perfectly reflecting surfaces normal to the various parts of the jet of gas, reversing the velocities on collision, or could adopt some such device. But if the distribution of velocities is on too small a scale to see and work with, we have no hope of reversing the velocities experimentally. Considering our emulsion of black and white fluid, which we have produced by shaking, there is no mechanical reason why the fluid could not be unshaken, by exactly reversing all the motions that occurred in shaking it. But nobody would be advised to try the experiment.

It used to be considered possible to imagine a being of finer and more detailed powers of observation than ours, who could regulate systems on a smaller scale than we could. Such a being could reverse processes that we could not; to him, the definition of a reversible process would be different from what it is to us. Such a being was discussed by Maxwell and is often called "Maxwell's Demon." Is it possible, we may well ask, to



imagine demons of any desired degree of refinement? If it is, we can make any arbitrary process reversible, keep its entropy from increasing, and the second law of thermodynamics will cease to have any significance. The answer to this question given by the quantum theory is No. An improvement in technique can carry us only a certain distance, a distance practically reached in plenty of modern experiments with single atoms and electrons, and no conceivable demon, operating according to the laws of nature, could carry us further. The quantum theory gives us a fundamental size of cell in the phase space, such that we cannot regulate the initial conditions of an assembly on any smaller scale. And this fundamental cell furnishes us with a unique way of defining entropy and of judging whether a given process is reversible or irreversible.

**5. The Canonical Assembly.**—In the preceding section, we have shown that our entropy, as defined in Eq. (1.2), has one of the properties of the physical entropy: it increases in an irreversible process, for it increases whenever the assembly becomes diffused or scattered, and this happens in irreversible processes. We must next take up thermal equilibrium, finding first the correct assembly to describe the density function in thermal equilibrium, and then proving, from this density function, that our entropy satisfies the condition  $dS = dQ/T$  for a reversible process. From Liouville's theorem, we have one piece of information about the assembly: in order that it may be independent of time, the quantity  $f_i$  must be a function only of the energy of the system. We let  $E_i$  be the energy of a system in the  $i$ th cell, choosing for this purpose the type of quantum cells representing stationary states or energy levels. Then we wish to have  $f_i$  a function of  $E_i$ , but we do not yet see how to determine this function.

The essential method which we use is the following: We have seen that in an irreversible process, the entropy tends to increase to a maximum, for an assembly of isolated systems. If all systems of the assembly have the same energy, then the only cells of phase space to which systems can travel in the course of the irreversible process are cells of this same energy, —a finite number. The distribution of largest entropy in such a case, as we have seen in Sec. 1, is that in which systems are distributed with uniform density through all the available cells. This assembly is called the microcanonical assembly, and it satisfies our condition that the density be a function of the energy only: all the  $f_i$ 's of the particular energy represented in the assembly are equal, and all other  $f_i$ 's are zero. But it is too specialized for our purposes. For thermal equilibrium, we do not demand that the energy be precisely determined. We demand rather that the temperature of all systems of the assembly be the same. This can be interpreted most properly in the following way. We allow each system of the assembly to be in contact with a temperature bath of

the required temperature, a body of very large heat capacity held at the desired temperature. The systems of the assembly are then not isolated. Rather, they can change their energy by interaction with the temperature bath. Thus, even if we started out with an assembly of systems all of the same energy, some would have their energies increased, some decreased, by interaction with the bath, and the final stable assembly would have a whole distribution of energies. There would certainly be a definite average energy of the assembly, however; with a bath of a given temperature, it is obvious that systems of abnormally low energy will tend to gain energy, those of abnormally high energy to lose energy, by the interaction. To find the final equilibrium state, then, we may ask this question: what is the assembly of systems which has the maximum entropy, subject only to the condition that its mean energy have a given value? It seems most reasonable that this will be the assembly which will be the final result of the irreversible contact of any group of systems with a large temperature bath.

The assembly that results from these conditions is called the canonical assembly. Let us formulate the conditions which it must satisfy. It must be the assembly for which  $S = -k \sum_i f_i \ln f_i$  is a maximum, subject

to a constant mean energy. But we can find the mean energy immediately in terms of our distribution function  $f_i$ . In the  $i$ th cell, a system has energy  $E_i$ . The fraction  $f_i$  of all systems will be found in this cell. Hence the weighted mean of the energies of all systems is

$$U = \sum_i E_i f_i. \quad (5.1)$$

This quantity must be held constant in varying the  $f_i$ 's. Also, as we saw in Eq. (1.1), the quantity  $\sum_i f_i$  equals unity. This must always be satisfied, no matter how the  $f_i$ 's vary. We can restate the conditions, by finding  $dS$  and  $dU$ : we must have

$$dS = 0 = -k \sum_i df_i (\ln f_i + 1), \quad (5.2)$$

for all sets of  $df_i$ 's for which simultaneously

$$dU = 0 = \sum_i df_i E_i, \quad (5.3)$$

and

$$0 = \sum_i df_i. \quad (5.4)$$

On account of Eq. (5.4), we can rewrite Eq. (5.2) in the form

$$dS = 0 = -k \sum_i df_i \ln f_i. \quad (5.5)$$

The set of simultaneous equations (5.3), (5.4), (5.5) can be handled by the method called undetermined multipliers: the most general value which  $\ln f_i$  can have, in order that  $dS$  should be zero for any set of  $df_i$ 's for which Eqs. (5.3) and (5.4) are satisfied, is a linear combination of the coefficients of  $df_i$  in Eqs. (5.3) and (5.4), with arbitrary coefficients:

$$\ln f_i = a + bE_i. \quad (5.6)$$

For if Eq. (5.6) is satisfied, Eq. (5.5) becomes

$$\begin{aligned} dS &= -k \sum_i df_i (a + bE_i) \\ &= -ka \sum_i df_i - kb \sum_i df_i E_i, \end{aligned} \quad (5.7)$$

which is zero for any values of  $df_i$  for which Eqs. (5.3) and (5.4) are satisfied.

The values of  $f_i$  for the canonical assembly are determined by Eq. (5.6). It may be rewritten

$$f_i = e^{a+bE_i}. \quad (5.8)$$

Clearly  $b$  must be negative; for ordinary systems have possible states of infinite energy, though not of negatively infinite energy, and if  $b$  were positive,  $f_i$  would become infinite for the states of infinite energy, an impossible situation. We may easily evaluate the constant  $a$  in terms of  $b$ , from the condition  $\sum_i f_i = 1$ . This gives at once

$$\begin{aligned} e^a \sum_i e^{bE_i} &= 1, \\ e^a &= \frac{1}{\sum_j e^{bE_j}}, \end{aligned}$$

so that

$$f_i = \frac{e^{bE_i}}{\sum_j e^{bE_j}}. \quad (5.9)$$

If the assembly (5.9) represents thermal equilibrium, the change of entropy when a certain amount of heat is absorbed in a reversible process

should be  $dQ/T$ . The change of entropy in any process in thermal equilibrium, by Eqs. (5.5) and (5.9), is

$$\begin{aligned} dS &= -k \sum_i df_i \ln f_i = -k \sum_i df_i (bE_i - \ln \sum_j e^{bE_j}) \\ &= -kb \sum_i df_i E_i, \end{aligned} \quad (5.10)$$

using Eq. (5.4). Now consider the change of internal energy. This is

$$dU = \sum_i (E_i df_i + f_i dE_i). \quad (5.11)$$

The first term in Eq. (5.11) arises when the external forces stay constant, resulting in constant values of  $E_i$ , but there is a change in the assembly, meaning a shift of molecules from one position and velocity to another. This change of course is different from that considered in Eq. (5.3), for that referred to an irreversible approach to equilibrium, while this refers to a change from one equilibrium state to another of different energy. Such a change of molecules on a molecular scale is to be interpreted as an absorption of heat. The second term, however, comes about when the  $f_i$ 's and the entropy do not change, but the energies of the cells themselves change, on account of changes in external forces and in the potential energy. This is to be interpreted as external work done on the system, or the negative of the work done by the system. Thus we have

$$dQ = \sum_i E_i df_i, \quad dW = -\sum_i f_i dE_i. \quad (5.12)$$

Combining Eq. (5.12) with Eq. (5.11) gives us the first law,

$$dU = dQ - dW.$$

Combining with Eq. (5.10), we have

$$dS = -kb dQ. \quad (5.13)$$

Equation (5.13), stating the proportionality of  $dS$  and  $dQ$  for a reversible process, is a statement of the second law of thermodynamics for a reversible process, if we have

$$-kb = \frac{1}{T}, \quad b = -\frac{1}{kT}. \quad (5.14)$$

Using Eq. (5.14), we can identify the constants in Eq. (5.9), obtaining as the representation of the canonical assembly

$$f_i = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}}. \quad (5.15)$$

It is now interesting to compute the Helmholtz free energy  $A = U - TS$ . This, using Eqs. (5.1) and (5.15), is

$$\begin{aligned} A &= \sum_i f_i \left( E_i - E_i - kT \ln \sum_j e^{-\frac{E_j}{kT}} \right) \\ &= -kT \ln \sum_j e^{-\frac{E_j}{kT}}, \end{aligned} \quad (5.16)$$

or

$$e^{-\frac{A}{kT}} = Z = \sum_j e^{-\frac{E_j}{kT}}. \quad (5.17)$$

Using Eq. (5.17), we may rewrite the formula (5.15) as

$$f_i = e^{-\frac{(A-E_i)}{kT}}. \quad (5.18)$$

The result of Eq. (5.17) is, for practical purposes, the most important result of statistical mechanics. For it gives a perfectly direct and straightforward way of deriving the Helmholtz free energy, and hence the equation of state and specific heat, of any system, if we know its energy as a function of coordinates and momenta. The sum of Eq. (5.17), which we have denoted by  $Z$ , is often called the partition function. Often it is useful to be able to derive the entropy, internal energy, and specific heat directly from the partition function, without separately computing the Helmholtz free energy. For the entropy, using

$$S = -\left(\frac{\partial A}{\partial T}\right)_v,$$

we have

$$S = \left\{ \frac{\partial}{\partial T} (kT \ln Z) \right\}_v = k \ln Z + \frac{kT}{Z} \left( \frac{\partial Z}{\partial T} \right)_v \quad (5.19)$$

For the internal energy,  $U = A + TS$ , we have

$$\begin{aligned} U &= -kT \ln Z + kT \ln Z + \frac{kT^2}{Z} \left( \frac{\partial Z}{\partial T} \right)_v \\ &= \frac{kT^2}{Z} \left( \frac{\partial Z}{\partial T} \right)_v \\ &= \left( \frac{\partial \ln Z}{\partial \left( \frac{-1}{kT} \right)} \right)_v, \end{aligned} \quad (5.20)$$

where the last form is often useful. For the specific heat at constant

volume, we may use either  $C_V = (\partial U / \partial T)_V$  or  $C_V = T(\partial S / \partial T)_V$ . From the latter, we have

$$C_V = T \left( \frac{\partial^2 (kT \ln Z)}{\partial T^2} \right)_V. \quad (5.21)$$

We have stated our definitions of entropy, partition function, and other quantities entirely in terms of summations. Often, however, the quantity  $f_i$  changes only slowly from cell to cell; in this case it is convenient to replace the summations by integrations over the phase space. We recall that all cells are of the same volume,  $h^n$ , if there are  $n$  coordinates and  $n$  momenta in the phase space. Thus the number of cells in a volume element  $dq_1 \dots dq_n dp_1 \dots dp_n$  of phase space is

$$\frac{dq_1 \dots dp_n}{h^n}.$$

Then the partition function becomes

$$Z = \left( \frac{1}{h^n} \right) \int \dots \int e^{-\frac{E}{kT}} dq_1 \dots dp_n, \quad (5.22)$$

a very convenient form for such problems as finding the partition function of a perfect gas.