

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 1.379×10^{-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.

Boltzmann¹ 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 . Planck² 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).

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

² 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.¹ 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

¹For 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 Δq_1 along the axis representing the first coordinate, Δq_2 for the second coordinate, and so on up to Δq_N for the N th coordinate, and Δp_1 to Δp_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 6.61×10^{-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 ν 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 πab ; 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 θ , and the corresponding momentum p_θ is the angular momen-

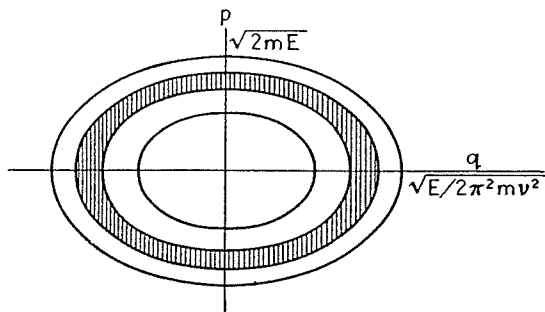


FIG. III-1.—Cells in phase space, for the linear oscillator. The shaded area, between two ellipses of constant energy, has an area h in the quantum theory.

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_θ . Since θ goes from zero to 2π , 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

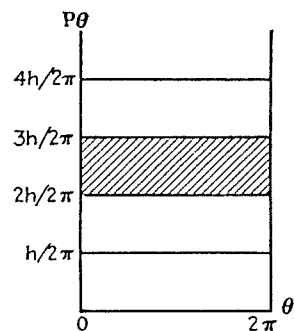


FIG. III-2.—Cells in phase space, for the rotator. The shaded area has an area of h in the quantum theory.

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 Gibbs¹ 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

¹J. 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

$$\frac{dq_1 \dots dq_n dp_1 \dots dp_n}{h^n}.$$

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.