

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]  
**GENERALIZED THERMODYNAMICS INCLUDING THE THEORY  
OF FLUCTUATIONS**

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In the present paper I shall assume without discussion the conservation of energy, at least in the sense in which this principle is used in thermodynamics. I shall not discuss the various discoveries of quantum theory which have exerted so great an influence upon present scientific thought. To these subjects I may later revert, but at present I wish to examine only those ideas which have been in the minds, almost since the beginning of thermodynamics, of those who have been troubled by the contradiction between the second law of thermodynamics and the existence of the so-called fluctuations which many systems exhibit, and which it is believed that more and more systems will exhibit as our means of measurement become more refined.

Willard Gibbs, in his early paper, first showed the incompatibility between molecular theory and the statement of classical thermodynamics that every system proceeds steadily toward a unique final state. We now have abundant experimental evidence also that a system left to itself for an indefinite time assumes no single equilibrium state, but passes back and forth through a great number of different states which, however, are not easily distinguishable.

Therefore classical thermodynamics, although admittedly invalid, is an extremely good first approximation to the truth. The second approximation, indicated abstractly in Gibbs' "Statistical Mechanics," was given concrete expression by Einstein,<sup>1</sup> who combined the first approximation given by classical thermodynamics with the famous theorem of Boltzmann relating entropy and probability. He thus obtained an equation which is of great value in determining the probability that any one observation will lie within a given range of fluctuation.

Our science is therefore in a position in which it is able to give an answer with almost any desired accuracy to any problem, not only of the older thermodynamics, but also of the theory of fluctuations. But since the science is not quite exact it fails to satisfy our logical desires and also our pedagogic needs, for no valid statement of the second law of thermodynamics has as yet been formulated.

I have long sought the proper way to place thermodynamics upon an exact basis, deriving the laws corresponding to those of classical thermodynamics, as well as the laws of fluctuations, from a single postulate. The task, however, has been a puzzling one and only in recent years have I perceived how

<sup>1</sup> Einstein, *Ann. Physik*, 22, 569 (1907).

simple the solution really is. The problems in which the second law of thermodynamics has been employed are all concerned with the partition of some quantity, such as energy, or some kind of matter, between several systems. We may begin our discussion with the study of such partitions.

Before proceeding with the analysis it may not be superfluous to point out that even when a mathematical science is made mathematically and logically exact, it is not precisely applicable to any actual physico-chemical system. It corresponds rather to an ideal system which may be regarded as a limit toward which actual systems can be made to approach as near as we please. Such a limit is implied when we define an *isolated* system as one which is cut off from all other systems with respect to the passage of matter or energy. In this sense we speak of completely impermeable walls, perfect mirror surfaces and the like.

In a similar way we define *independent* systems as those which do not influence the thermodynamic properties of one another by their mere propinquity. Thus two bottles of water become more nearly independent as they are separated spatially, and even the upper and lower halves in the same bottle may be regarded as nearly independent since, owing to the small range of molecular forces, only a very little of one part is much influenced by the other. On the other hand, in dealing with surface phenomena we are often obliged to discuss systems which are far from independent.

A similar idealization is necessary when we discuss equilibrium. If we are studying the relation between the pressure and volume of a mixture of oxygen and hydrogen at  $0^\circ$ , we ignore the fact that the two gases are very slowly combining to form water. If we are measuring the solubility of potassium chloride, we forget that at the end of a trillion years a considerable part of the potassium will have suffered radioactive decay. So in our idealized system we assume that certain specified processes occur at a rate which is infinitely greater than that of all other processes. The former may be spoken of as *permitted* and the latter as *prohibited* processes. In our present treatment of thermodynamics we may replace the idea of the time required for the attainment of equilibrium by the idea of the time sufficient to give a representative statistical sample of all the permitted states of a system. This length of time, however, does not enter directly into our considerations, and, indeed, time is not one of the variables with which pure thermodynamics is concerned.<sup>2</sup>

### Partition Between Two or More Systems

Let us consider the partition of some quantity  $X$  between two independent systems. This quantity  $X$  may be the energy, of some chemical substance, or, if the two systems are separated by a movable partition, it may be the volume. If such a partition varies from time to time it will not be our present duty to seek the cause; whether the individual parts of the system follow the old mechanics, or the new mechanics, or no mechanics at all, need not concern us now.

If we wish to study some momentary partition we fix or "freeze" that partition by interrupting communication between the two systems.<sup>3</sup>

<sup>2</sup> Lewis, "The Symmetry of Time," *Science*, 71, 569 (1930).

<sup>3</sup> I have considered it sufficient in the present paper to state what seems to me true, without explicitly correcting some false ideas that have crept into thermodynamic literature. However, there is one thing that must be said to avoid serious confusion. If the thermodynamic properties of a system, such as temperature, entropy and pres-

In other words, we isolate them from one another and then we may proceed to determine experimentally what the content of the quantity  $X$  is in the system I and in the system II. If such a determination is made from time to time and the results are recorded, they may not permit a satisfactory prediction of what partitions will occur in the future, but if the intervals between the observations, and also their number, are increased without limit, our data may be said to become representative, in the sense that the fraction of all partitions lying within a given range may be equated to the probability that any new observation will lie within that range.

Instead of having our systems I and II isolated from all others, we may have a third system which we may call a reservoir, in communication with these two, and this reservoir may be considered capable of being increased indefinitely in size (without changing its intensive properties, such as density, composition and density of energy). Now when the quantity  $X$  is partitioned between these three systems, the probability that the content of  $X$  in system I will lie between  $C_1$  and  $C_1 + \lambda$  may be designated by  $\alpha_1\lambda$ , while  $\alpha_2\lambda$  will express the probability that the content in system II lies between  $C_2$  and  $C_2 + \lambda$ . If  $\lambda$  be chosen indefinitely small, there will be the same probability that the content in system II will lie in one or the other of the two equal and adjacent ranges,  $C_2$  to  $C_2 + \lambda$  and  $C_2$  to  $C_2 - \lambda$ . Henceforth we shall choose the latter expression on account of its convenience in the discussion of the distribution between two systems alone.

If the two systems are independent and if the reservoir be made indefinitely large, the probability that the content of system I lies between  $C_1$  and  $C_1 + \lambda$ , and at the same time that the content of system II lies between  $C_2$  and  $C_2 - \lambda$  is given by the expression<sup>4</sup>

$$P = \alpha_1 \alpha_2 \lambda^2 \quad (1)$$

where  $\alpha_1$  is now independent of the system II, and  $\alpha_2$  of the system I. While the range  $\lambda$  may be made as small as we please, having once chosen this range for a given quantity  $X$ , we shall regard it as constant throughout our equations.

sure, are to be unambiguously determined by certain independent variables such as the mass, the energy and the volume of a system, it follows that it is meaningless to say, for example, that the temperature of a system is the same or is not the same in all its parts. The temperature of an isolated system must have one and only one value. On the other hand, it is possible, with due caution, to assign a meaning to such a phrase. We may agree to say that the temperature of each part is the temperature it would have if it were suddenly isolated from the rest.

<sup>4</sup> If at the same time we wish to consider the partition of several quantities  $X$ ,  $Y$ ,  $Z$ , . . . , and choose  $\lambda_x$  as the range of the first quantity, and so on, the equation becomes

$$P = \alpha_1 \alpha_2 \lambda_x^2 \lambda_y^2 \lambda_z^2 \dots \quad (1a)$$

where the  $\alpha$ 's have the same meaning as before, except for a constant factor depending upon the chosen values of  $\lambda_y$ ,  $\lambda_z$ , etc. Since we gain in simplicity and lose nothing in generality, we shall continue to consider the partition of one quantity at a time.

If  $C_1'$  is another content of the first system and  $C_2'$  another content of the second system, but such that the total content is the same, namely,  $C_1' + C_2' = C_1 + C_2$ , the probability  $P'$  that the content of the first system will lie between  $C_1'$  and  $C_1' + \lambda$ , and *also* that the content of the second system will lie between  $C_2'$  and  $C_2' - \lambda$  is given by the corresponding expression

$$P' = \alpha_1' \alpha_2' \lambda^2$$

The ratio of the probabilities of the two partitions is then

$$\frac{P}{P'} = \frac{\alpha_1 \alpha_2}{\alpha_1' \alpha_2'} \quad (2)$$

The product  $\alpha_1 \alpha_2$  which belongs to a certain pair of systems with contents  $C_1$  and  $C_2$  may be called the *specific probability*, while the  $\alpha$ 's may be called the *probability factors*.

We are now in a position to state the cardinal postulate which is designed to validate, and at the same time to generalize, the second law of thermodynamics, and from which the laws of thermodynamics and the laws of fluctuations may both be derived. However, before making this postulate, it may be well to make certain comments which may serve to display its character and contribute to its plausibility.

When we have spoken of two systems as connected we have said nothing concerning the mode of connection. If we were considering a gas distributed between two vessels, they might be joined by a very narrow tube, or a very large one. If we were considering the passage of heat, the systems might be connected by a rod of very low or very high thermal conductivity. In any case, if the connection is a poor one and, having determined some partition, we soon after determine the partition once more, these two partitions will be almost the same. We have tried to eliminate such effects by making infinitely long the interval between two partition measurements, but that we have succeeded in making the relative probability of the various partitions independent of the mode of connection of the systems is, after all, an assumption which must be embodied in our fundamental postulate.

When we consider two systems and a reservoir we might make the connection between the two systems so good, and the connection between each system and the reservoir so poor, that during a time which is long enough to be almost completely representative with respect to all possible partitions between the two systems, there would be almost no exchange with the reservoir. In such case we should expect that the probability of the several partitions of the quantity  $X$  in the two systems would depend only upon the total amount of  $X$  in the two systems, and not at all upon the nature of the reservoir. Thus if the two systems were in very poor thermal contact with a reservoir and at a certain time the two systems should contain  $E$  units of energy, then if the same two systems were in poor contact with another reservoir, for example one of much higher temperature,

but if as a result of some rare fluctuation the total content of energy in the two systems were again  $E$ , then we should expect the laws of partition of this quantity  $E$  between the two systems to be the same in both cases.

**The Cardinal Postulate.**—Plausible as these ideas may be, they must be embodied in a formal postulate which will serve as a generalization of the second law of thermodynamics. This postulate is as follows: *when a given content is partitioned between two systems, the ratio of the specific probabilities of any two partitions of this content depends solely upon the nature of the two systems and upon the respective contents.* In other words, such a ratio as occurs in Equation 2 depends in no way upon the mode of connection between the systems nor upon the existence, or nature, or mode of connection of other systems.

It is evident from the way in which the probability factors were first introduced that each  $\alpha$  depends upon the kind of reservoir chosen, and upon the amount that it contains of the quantity whose partition is being studied, but it now follows from our postulate that the *relative* values of  $\alpha$  for a given system are independent of such choices. Aside then from an undetermined, and for the present purposes unimportant, constant multiplier, each  $\alpha$  depends solely upon a system and its content. It is therefore a corollary of our postulate that the specific probability for a given partition is (except for the undetermined constant) the product of two factors, one of which depends solely upon the first system and its content, the other solely upon the second system and its content. This corollary might itself have been taken as the generalization of the second law of thermodynamics and then our fundamental postulate would have appeared as a corollary.

In order to apply the methods of the differential calculus it would be convenient if  $\alpha$  for any system could be regarded as a continuous function of its content, but in some cases at least we know that the content cannot be varied continuously. Thus we cannot take from the system less than one atom of any element. Nevertheless, we usually approach very close to the limiting case in which the loss of one atom produces the same change in the thermodynamic properties of a system as the loss of a second atom, or a third, thus justifying the use of the differential calculus. In the present paper we shall restrict ourselves to the case in which the calculus is applicable, reserving the more general case for a later occasion.

By the aid of the calculus we may write down immediately the probability that a partition of a certain content will lie within a certain range, divided by the probability that a second partition of the same content will lie within another given range. Let the total content,  $C$ , be the same in both cases and let the specification of the first range be that  $C_1$  lies between  $a$  and  $b$  (and therefore that  $C_2$  lies between  $C-a$  and  $C-b$ ), while the corresponding specification for the second range is that  $C_1$  lies between  $a'$  and  $b'$ . The ratio of the two probabilities is then given by the formula

$$\frac{P}{P'} = \frac{\int_a^b \alpha_1 \alpha_2 dC_1}{\int_{a'}^{b'} \alpha_1 \alpha_2 dC_1} \quad (3)$$

where  $dC_1 = -dC_2$ . If we wish to make the second range cover all possible values, we obtain as the *absolute* probability that a partition lies within the range  $C_1 = a$  to  $C_1 = b$

$$P = \frac{\int_a^b \alpha_1 \alpha_2 dC_1}{\int_0^C \alpha_1 \alpha_2 dC_1} \quad (4)$$

These equations will enable us to solve any problem in the theory of fluctuations, as soon as  $\alpha_1$  is known as a function of  $C_1$ , and  $\alpha_2$  as a function of  $C_2$ , or  $C - C_1$ .

### The Most Probable Partition

In classical thermodynamics some minor assumptions are made in order to eliminate certain cases which, if they ever existed, would have to be treated separately (corresponding to certain zero cases in mathematics). Thus it is assumed, at any finite temperature, that the solubility of one substance in another is always finite, and that the heat capacity of any substance is also finite. Our corresponding assumption is that the most probable partition of any quantity between two systems is not the one in which the whole content is in one system. If such a case did occur it would require a separate treatment.

If then we have a quantity  $X$  in total amount  $C$ , divided between two systems, there must be some one partition at which the specific probability  $\alpha_1 \alpha_2$  has at least as high a value as at any other, and since this most probable partition does not lie at  $C_1 = 0$  or  $C_1 = C$ , it has the characteristics of a maximum. If  $\alpha_1 \alpha_2$  is at a maximum, its logarithm is also, and satisfies the condition

$$d \ln \alpha_1 \alpha_2 = d \ln \alpha_1 + d \ln \alpha_2 = 0 \quad (5)$$

If some one quantity whose content is  $C = C_1 + C_2$ , can vary alone, then

$$\frac{\partial \ln \alpha_1}{\partial C_1} dC_1 + \frac{\partial \ln \alpha_2}{\partial C_2} dC_2 = 0 \quad (6)$$

or since  $dC_1 = -dC_2$

$$\frac{\partial \ln \alpha_1}{\partial C_1} = \frac{\partial \ln \alpha_2}{\partial C_2} \quad (7)$$

This is the simplest expression of the condition that  $C_1$  and  $C_2$  represent the most probable partition of the total content  $C$ . This is the partition which is represented by the grossly exaggerated curve shown in Fig. 1.<sup>5</sup>

<sup>5</sup> Aside from the case illustrated in Fig. 1, there is only one other way in which  $\alpha_1 \alpha_2$  can be at a maximum, that is, when  $\alpha_1$  diminishes with increasing  $C_1$  and  $\alpha_2$  with diminishing  $C_2$ . It sometimes happens that this case also has thermodynamic interest, but we need not dwell on this question here, since what we have to say will be true of either case.

Our new thermodynamics makes distinctions which are not made in the older thermodynamics. In the latter there was just one equilibrium partition which was, of course, not only the most probable, but also the average partition. If we now recognize what was formerly called equilibrium, not as a single partition, but as a narrow region into which a vast number of individual partitions are crowded, the most probable partition will not

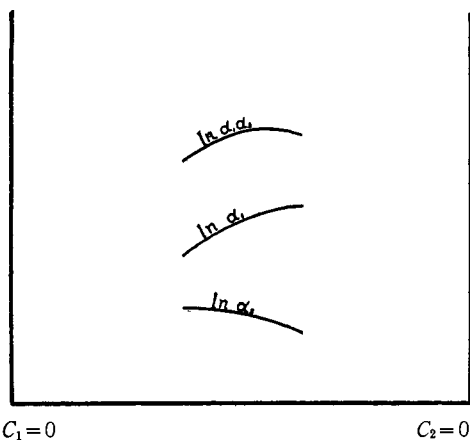


Fig. 1.

always exactly coincide with the average partition. It is characteristic of our present method of treatment that it is the most probable partition and not the average partition which we must now employ to represent the equilibrium. Henceforth when we say that two systems are in equilibrium we shall mean that for every variable quantity that can be divided between the two systems, the two contents correspond to the most probable partition. We then obtain directly from Equation 7 the important

law that *when two systems are in equilibrium with a third system, they are in equilibrium with each other.*

**The Thermodynamic Temperature.**—If it is the energy whose partition between two systems is being studied, the equation for thermal equilibrium is

$$\frac{\partial \ln \alpha_1}{\partial E_1} = \frac{\partial \ln \alpha_2}{\partial E_2} \quad (8)$$

Let us define  $\Theta$  by the equations

$$\frac{\partial \ln \alpha_1}{\partial E_1} = \frac{1}{\Theta_1}, \quad \frac{\partial \ln \alpha_2}{\partial E_2} = \frac{1}{\Theta_2} \quad (9)$$

At equilibrium  $\Theta_1 = \Theta_2$ , but if we depart from equilibrium in such a direction that  $E_1$  is less and  $E_2$  is greater than the values at the most probable partition, then we might show, from a study of the second derivative of  $\ln \alpha_1 \alpha_2$ , that  $\Theta_2$  cannot be less than  $\Theta_1$ . Hence  $\Theta$  obeys the qualitative laws of temperature, and might be defined as the thermodynamic temperature.

**Combination of Abstract Thermodynamics with Experimental Knowledge.**—We have now set forth all the essential abstract principles of generalized thermodynamics. In developing them I have endeavored to proceed with the utmost logical rigor. As we now approach the task of applying our abstract science to actual systems, we may afford to be a little more informal, since there are endless ways of making contact between our

theoretical principles and experimnt, and the choice of a particular method of making such contact will be largely a matter of taste.

There is nothing indeed in our preceding development which could possibly enable us to calculate for any physical system how its  $\ln \alpha$  changes with the several thermodynamic variables. To obtain such information we must either make some experimental study of a system, or some deduction concerning an idealized system based on generalizations of actual experiments. If one is interested in what is called statistical mechanics, it is at this point, and no earlier point, that the special laws of mechanics should be introduced.

At the corresponding stage in classical thermodynamics it is customary to introduce the properties of the actual substance, or rather that idealization of an actual substance, that we call the perfect gas. Thus, for example, the thermodynamic temperature is compared with the temperature recorded by a perfect gas thermometer. There are, however, many equally good ways of introducing the empirical properties of substances. Thus, in place of a gas thermometer we might use as a measure of temperature the potential of the galvanic cell, or the volume of a crystal, or the pressure of a Hohlraum.

We shall choose as our thermometer an idealized system composed of  $N$  similar molecules which for simplicity we may assume to be fixed in position, far apart, and subject to no change except that each molecule can exist in either of two states differing in energy by the amount  $\epsilon$ . Thus the energy of the system over that of the same system with all molecules in the lower state is

$$E = M\epsilon \quad (10)$$

where  $M$  is the number of molecules in the higher state. Then  $N - M$  are in the lower state, and we may define the temperature  $T$  by the equation

$$\frac{M}{N - M} = e^{-\epsilon/kT} \quad (11)$$

The classical work of van't Hoff and Boltzmann showed that this temperature scale may be identified with that of the perfect gas thermometer.

We shall now make the simple *assumption* that no molecule is more likely to be in the higher state than any other molecule. Let us arbitrarily divide the  $N$  molecules into two systems, the first having  $N_1$  and the second  $N_2$  molecules. Suppose that  $M_1$  of the former and  $M_2$  of the latter are in the higher energy state. If now by some method which need not be specified there is a flow of energy from the first system to the second, then  $M_1$  diminishes and  $M_2$  increases so that  $M_1' + M_2' = M_1 + M_2$ . According to our assumption the relative probabilities of these two partitions is equal to the relative number of ways in which the two partitions can be obtained.

The number of ways in which we may have the  $M$  units of energy



distributed among  $N$  molecules is the number of ways in which  $M$  unnumbered objects can be placed in  $N$  numbered boxes, no more than one to a box. It is  $N!/(M!(N-M)!)$ , so that the relative probability of the two partitions is

$$\frac{P}{P'} = \frac{\frac{N_1!}{M_1!(N_1 - M_1)!} \frac{N_2!}{M_2!(N_2 - M_2)!}}{\frac{N_1!}{M_1'!(N_1 - M_1')!} \frac{N_2!}{M_2'!(N_2 - M_2')!}} \quad (12)$$

Each of the four quotients appearing in the last member depends only upon a single system and its content. These quotients satisfy all the rules that we have laid down for our probability factors and each therefore is to be identified with the corresponding  $\alpha$ . Thus we find in general for this type of thermometric system

$$\alpha = \frac{N!}{M!(N - M)!} \quad (13)$$

and

$$\ln \alpha = \ln N! - \ln M! - \ln (N - M)! \quad (14)$$

If again we have the same  $N$  molecules, but  $M + 1$  in the higher level, we may bear in mind that

$$\ln (M + 1)! = \ln M! + \ln (M + 1); \quad \ln (N - M - 1)! = \ln (N - M)! - \ln (N - M)$$

and say that  $\ln \alpha$  has been increased by

$$\Delta \ln \alpha = -\ln (M + 1) + \ln (N - M) \quad (15)$$

Let us make the system large enough and  $M$  great enough so that  $M$  can be used in place of  $M + 1$ . Using the differential notation we have

$$\frac{\partial \ln \alpha}{\partial M} = \ln \frac{N - M}{M} \quad (16)$$

and now employing Equations 10 and 11 we find

$$\frac{\partial \ln \alpha}{\partial E} = \frac{1}{kT} \quad (17)$$

We see from Equation 17 that  $kT$  is equal to our thermodynamic temperature  $\Theta$ . Having proved this for one system, we have proved it for all, for if we have any other system in thermal equilibrium with our thermometric system so that the  $\Theta$  and  $T$  are the same for both, and if  $\Theta = kT$  for one system, this is also true of the other.

If we are dealing with a pure substance under such conditions that the properties of a given mass are completely determined by its energy and volume, all that we need to know further about  $\ln \alpha$  is the way it changes with the volume. Here also we must make use of some empirical information. We may take it as experimentally established that any physico-chemical equilibrium which is obtained on the first floor of a laboratory will not be changed by taking the whole system to the second floor. This means that if the various  $\alpha$ 's change with the height, they all change in the same proportion. Since the  $\alpha$ 's already contain undetermined factors,

we may say that the  $\alpha$  for each system is independent of its position in a constant gravitational field.

Let us consider a cylinder divided into two parts by a movable piston of unit area and of weight  $P$ . The lower part, or system I, contains any substance whose properties are determined solely by the energy and the volume. The upper part, or system II, is exhausted and contains only the piston. As the height of the piston<sup>6</sup> fluctuates there will be one position that is most probable. At this equilibrium position we may say that the pressure in system I is equal to the pressure  $P$  exerted by the piston. When this position of equilibrium is reached  $d \ln \alpha$ , by Equation 5, will be numerically the same for the two systems, but according to our assumption  $d \ln \alpha$  is zero for the upper system, and therefore is also for the lower system. Hence for the latter

$$d \ln \alpha = 0 = \frac{\partial \ln \alpha}{\partial V} dV + \frac{\partial \ln \alpha}{\partial E} dE \quad (18)$$

By applying the first law of energy to this system

$$dE = -P dV$$

Combining the last two equations with Equation 17, we find for any system whose properties are determined by energy and volume

$$\frac{\partial \ln \alpha}{\partial V} = \frac{P}{kT} \quad (19)$$

**Entropy, and its Use in Calculating Fluctuations.**—If we compare Equations 17 and 19 with those which in classical thermodynamics completely define the entropy, namely

$$\frac{\partial S}{\partial E} = \frac{1}{T} \quad \frac{\partial S}{\partial V} = \frac{P}{T}$$

we may immediately identify the entropy with  $k \ln \alpha$ , except for an undetermined additive constant, which need not concern us, since by our definition  $\ln \alpha$  is determined only to an additive constant, and this is also true for the classical entropy. Hence, in general, we write

$$S = k \ln \alpha \quad \alpha = e^{S/k} \quad (20)$$

We have now completely bridged the gap between the new and the old thermodynamics. It is true that we have made use only of a pure substance under such conditions that it is subject only to the variables, volume and energy. However, we may also consider the partition of any quantity between such a substance on the one hand, and on the other hand a substance which is in solution, or which depends upon other variables, such as electric and surface forces. The resulting equations will be the familiar

<sup>6</sup> In order to avoid the need of considering the kinetic energy of the piston we may make it as heavy as we please. Indeed, according to the principle of Heisenberg, it is only when the mass of the piston is infinite that we may assign to it zero velocity and also a fixed position.

equations of thermodynamics. To obtain them is a matter of mere routine. From the simple principles with which we started we have therefore obtained the whole of classical thermodynamics.

Moreover, we may now give an equally exact and more useful form of Equation 4. Substituting the values of  $\alpha$  from Equation 20, and writing  $S = S_1 + S_2$ , we have

$$P = \frac{\int_a^b e^S dC_1}{\int_0^C e^S dC_1} \quad (21)$$

This equation enables us to solve any problem regarding fluctuations when the entropies are known as functions of the several contents.

For practical purposes it usually suffices to know the value of  $S$ , not over the whole range from zero to  $C$ , but over a very small range in the neighborhood of the equilibrium point  $C_1 = C_1^\circ$ . Indeed by a familiar method we may obtain a very good approximation if we know only the second derivative of  $S$  with respect to  $C_1$  at this point. Dividing both numerator and denominator in Equation 21 by  $e^{S^\circ}$ , where  $S^\circ$  is the combined entropy of the two systems at the equilibrium point, the integrals with which we have to deal have the form

$$\int e^{S-S^\circ} dC_1$$

Now if  $S - S^\circ$  is developed by Taylor's formula in terms of  $C_1 - C_1^\circ$ , then, because of the existence of the maximum, the first term in the expansion will be the one containing the second derivative. Neglecting higher terms we have

$$S - S^\circ = \frac{1}{2} \frac{\partial^2 S}{\partial C_1^2} (C_1 - C_1^\circ)^2 \quad (22)$$

The integral with which we are dealing is now in the form of the well-known probability integral, for which there are satisfactory tables.

If we now compare these equations with those given by Einstein, we see a resemblance which becomes an identity if we subject his equations to the interpretation given in the present paper, of which the most important is the interpretation of the classical equilibrium as the partition of highest specific probability.

### Summary

By a method which differs radically from the methods used either in classical thermodynamics or in statistical mechanics, it is shown that the laws of thermodynamics and the laws of fluctuations constitute together a generalized thermodynamics which is derivable from a single cardinal postulate. It is claimed, moreover, that this postulate is the first really valid statement of the second law of thermodynamics.