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THE RELATION BETWEEN STATISTICAL MECHANICS AND THERMODYNAMICS.

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I. Introduction.

There have been two main methods of investigating the relation between statistical mechanics and thermodynamics, that of Gibbs and that of Boltzmann.

The method adopted by Gibbs was to study the properties of an ensemble of systems, each individual system of the ensemble being identical in structure with the actual physical-chemical system of interest. The systems of the ensemble were distributed in phase in accordance with the so-called canonical distribution law, and Gibbs was able to show that such a distribution is permanent and that the statistical-mechanical quantities determining this distribution have the properties of the thermodynamic quantities, free energy, energy, and temperature and was thus able to show in a very general and beautiful manner that the laws of thermodynamics are a natural consequence of statistical mechanics.

The method adopted by Boltzmann has been to consider a single physical-chemical system and study the distribution in phase of the molecules of this system when it has reached its configuration of maximum probability and hence of thermodynamic equilibrium. The law determining the distribution of the molecules in this state of equilibrium is known as the Maxwell-Boltzmann distribution law and although similar in form to the Gibbs canonical distribution law is not identical in content, since it deals with the distribution of molecules in a system instead of with the distribution of systems in an ensemble of systems. As to the relation between statistical mechanics and thermodynamics, Boltzmann has been able to show a fundamental connection between the probability of the configuration of the system at equilibrium and the entropy of the system and thus again to show that the laws of thermodynamics are a natural consequence of statistical mechanics.

The method of Boltzmann is perhaps somewhat less general than that of Gibbs, but leads perhaps more directly to very important information concerning the behavior of the individual molecules of the system. It is the method which will be adopted in this article.

Since Boltzmann, important investigations of the relation between the statistical mechanical quantity, probability, and the thermodynamic quantity, entropy, have been made by Planck. The work presented here will differ from that of Planck in two ways. In the first place, for the purpose of this article, we shall take no position with reference to the

quantum theory although the results obtained can easily be modified in accordance with the Planck quantum theory by assigning, as he does, a definite location and finite size G to the regions into which we divide the generalized space used in representing the phase of the individual molecules.¹ A more important difference between the method adopted in this article and that of Planck, is that instead of somewhat arbitrarily defining entropy, as a constant times the logarithm of probability, we shall endeavor to discover a statistical mechanical quantity which has the same derivatives with respect to the fundamental variables, energy E , volume v , and number of molecules N , as does entropy. This leads us to a somewhat different expression for entropy from that used by Planck, since the Planck expression although depending on the energy and volume in the correct manner does not make the entropy of a homogeneous system maintained at constant pressure and temperature vary proportionally to the number of molecules present. The Planck expression can be made to agree with ours by the addition of a term which is a function of the number of molecules present.²

¹ In another place (*Phys. Rev.*, 9, 261 (1918)) the writer has presented suggestions as to a method of reconciling quantum theory and statistical mechanics without giving up so much of the classical statistical mechanics as Planck has done.

² Many other investigators, besides Planck, have recently considered the relation between statistical mechanics and thermodynamics. Thus Marcelin, in his important contribution to the theory of physical chemical kinetics (*Ann. Phys.*, 3, 120 (1915)), has made use of a relation between free energy and a quantity occurring in the Maxwell-Boltzmann distribution law which the present writer believes to be incorrect. An article attempting to justify Marcelin's procedure has recently been published by E. P. Adams (*THIS JOURNAL*, 43, 1251 (1921)) but the present writer cannot agree with Adams' conclusions.

A comparison of equations obtained in this article with those obtained by Adams will show the lack of agreement. Expressing Maxwell's distribution law for a system of N molecules in the form

$$dN = e^{\frac{\psi - \epsilon}{kT}} dq_1 \dots dp_n$$

we shall obtain, in this article, for the Helmholtz free energy of the system, the expression

$$F = N\psi - N\bar{\epsilon} + E \quad (\text{Equation 35, this article})$$

while Adams obtains

$$F = N\psi. \quad (\text{Equation 10, } op. cit.)$$

The two equations become identical only for a perfect gas.

For the partial molal free energy of the substance involved, we shall obtain the expression

$$\left(\frac{\partial F}{\partial n} \right)_{v,T} = N_A \psi + RT. \quad (\text{Equation 39, this article})$$

where n is the number of mols and N_A is Avogadro's number, while Adams obtains $\partial F / \partial n = N_A \psi$. (See Equation 11 and preceding discussion, *op. cit.*)

The two equations are not even the same for the case of a perfect gas.

II. Derivation of the Maxwell-Boltzmann Distribution Law.

In order to obtain the desired conclusion, it will be necessary to review in a fundamental way the derivation of the Maxwell-Boltzmann distribution law

$$dN = Ce^{\frac{-\epsilon}{kT}} dq_1 \dots dp_n$$

where dN is the number of molecules having coördinates and momenta falling in the infinitesimal range $dq_1 \dots dp_n$. In particular we shall find it necessary to analyze with considerable care the meaning of the quantity ϵ when it first enters the discussion. We shall find in general that ϵ must be taken *not* as the energy of a molecule, having coördinates and momenta falling in a particular region $dq_1 \dots dp_n$, but *rather* as the rate of increase in the total energy of the system per molecule added to the region $dq_1 \dots dp_n$ when the system is in its configuration of maximum probability. These two quantities are the same for dilute gases but for concentrated systems may be quite different. Hence the new methods which we introduce will be of considerable importance in dealing with the properties of imperfect gases or other concentrated systems.

1. **The System.**—For the purposes of this article we shall merely consider systems containing molecules or elements of a single kind. The methods employed, however, can easily be generalized to cover systems containing molecules, atoms, modes of vibration and so forth of any number of different kinds. We shall assume that the instantaneous state or phase of the system is determined by a specification of the generalized coördinates and momenta and that it obeys the laws of dynamics expressed for example in the Hamiltonian form.

2. **Probability of a Given Microscopic State.**—If $Q_1 Q_2 \dots Q_m P_1 P_2 \dots P_m$ are generalized coördinates and momenta which can be used for describing the state of the system, we may think of the motion of the system as determined by the motion of a point in a $2m$ dimensional space corresponding to the $2m$ coördinates and momenta. We shall say that the *microscopic state* of the system at any instant is specified by a statement of the particular infinitesimal region of generalized space $dQ_1 dQ_2 \dots dQ_m, dP_1 dP_2 \dots dP_m$ in which the representative point for the system in question is to be found. *We shall consider all the different possible microscopic states for a given system as equally probable.*

The justification for this assumption of equal probability for the different possible microscopic states has usually been based, in considerations of this kind, on the possibility of showing with the help of the Hamiltonian laws of motion, that an ensemble of similar systems with representative points uniformly distributed throughout the generalized space will permanently retain this uniform distribution. For our present purposes we shall accept this justification as sufficient and not attempt at this

time a more fundamental analysis of this feature of the classical statistical mechanics.

3. **Probability of a Given Statistical State.**—Let N be the number of elements (molecules) which go to make up the complete physical-chemical system in which we are interested. And let our imaginary division of the system into elements and our choice of coördinates be so made that the original $2m$ generalized coördinates and momenta belonging to the whole system can be assigned to the individual elements of the system. Let $q_1q_2\dots q_n p_1p_2\dots p_n$ be the coördinates and momenta belonging to a single element. We shall be specially interested then in the number of elements which have values of coördinates and momenta falling in any particular infinitesimal region

$$d\sigma = dq_1dq_2\dots dq_ndp_1dp_2\dots dp_n \quad (1)$$

We shall say that the statistical state of our system is specified by a statement of the number of elements of the various kinds which have values of their coördinates and momenta which fall in the different possible infinitesimal regions $d\sigma$.

It will be seen that the *microscopic state* of the system determines the coördinates and momenta for each individual element of the system, while the *statistical state* merely determines the number of elements of each of the different kinds which have coördinates and momenta falling in a particular range, without attempting to make any distinction as to which particular elements are taken to supply the quota.

We thus see that corresponding to a given statistical state there will be a large number of microscopic states which can be obtained by the inter-transposition of elements from one infinitesimal region to another without disturbing the total number in each region. Since we have already taken the microscopic states as equally probable, *we shall take the probability of any given statistical state as proportional to the number of microscopic states to which it corresponds.*

Let us specify a given statistical state by taking $N_1N_2N_3\dots$ as the number of elements having coördinates and momenta falling in the particular infinitesimal regions $d\sigma_1, d\sigma_2, d\sigma_3, \text{ etc.}$

Then it is evident from the principles of permutation that the number of microscopic states corresponding to the given statistical state will be

$$W = \frac{|N|}{|N_1| |N_2| |N_3| \dots} \quad (2)$$

We shall call W the probability of the statistical state in question without introducing any proportionality factor.

Let us assume that each of the numbers $N, N_1, N_2, N_3, \text{ etc.}$, occurring in Equation 2 is large enough so that we may apply the Stirling formula for factorial N

$$\sqrt{N} = \sqrt{2\pi N} \left(\frac{N}{e} \right)^N \quad (3)$$

Substituting in Equation 2, taking the logarithm of W and omitting negligible terms we obtain

$$\log W = N \log N - N_1 \log N_1 - N_2 \log N_2 \dots \quad (4)$$

which can be rewritten in the form

$$\log W = N \log N - \Sigma N_i \log N_i \quad (5)$$

where the summation Σ is to be taken over all the infinitesimal regions $i=1,2,3,\dots$.

4. Statistical State of Maximum Probability.—We shall be particularly interested in the statistical state of maximum probability which our system can assume with a *given number of molecules*, a *given energy content* and a *given volume*. Our interest in this state of maximum probability is due to the fact that we shall consider the system to be substantially in its state of maximum probability when thermodynamic equilibrium is attained.

Considering Equation 5, it is evident that the condition of maximum probability will be

$$\delta \log W = \delta \{ N \log N - \Sigma N_i \log N_i \} = 0 \quad (6)$$

This variation is not to be carried out entirely arbitrarily, however, since as stated above we shall not allow the number of molecules, the energy content nor the volume of the system to change.

Since the number of molecules is not to change we shall have

$$\delta N = \Sigma \delta N_i = 0 \quad (7)$$

As to the energy of the system E , it is evident that this is a function of the number of molecules N_1, N_2, N_3, \dots in each of the infinitesimal regions, and since this is to be constant we may write

$$\delta E = \Sigma \frac{\partial E}{\partial N_i} \delta N_i = 0 \quad (8)$$

As to the constancy of volume this is a matter of great importance since three of the coördinates q_1, \dots, q_n must necessarily correspond to the location of the infinitesimal region $d\sigma$ in ordinary three-dimensional space, and hence if the volume of the container were varied this would lead to a variation in the total volume of the generalized $2n$ -dimensional space σ and hence in the number of infinitesimal regions $d\sigma_1, d\sigma_2, d\sigma_3$, etc. Under the present circumstances we shall not be bothered with this possibility.

The simultaneous Equations 6, 7 and 8 may now be combined by the method of undetermined multipliers, giving us,

$$\Sigma \{ (\log N_i + 1) \delta N_i + \lambda \delta N_i + \mu \frac{\partial E}{\partial N_i} \delta N_i \} = 0$$

or

$$\Sigma \{ \log N_i + 1 + \lambda + \mu \frac{\partial E}{\partial N_i} \} \delta N_i = 0 \quad (9)$$

where the quantities λ and μ are undetermined multipliers. Since the introduction of these multipliers makes the variations δN_i entirely arbitrary, it is evident that Equation 9 can only be true if the individual equations

$$\log N_i + 1 + \lambda + \mu \frac{\partial E}{\partial N_i} = 0 \quad (10)$$

are also true.

These equations can be put in a more convenient and familiar form if we introduce some different symbols. Let us put

$$\partial E / \partial N_i = \epsilon_i \quad (11)$$

$$\mu = 1/\theta \quad (12)$$

$$1 + \lambda = -\Psi/\theta \quad (13)$$

where the new symbols are defined by the equations given.

Substituting in (10) and solving for N_i we obtain

$$N_i = e^{\frac{\Psi - \epsilon_i}{\theta}} \quad (14)$$

This is an expression for the number of molecules whose coördinates and momenta fall in the i 'th infinitesimal region $d\sigma_i$ when the distribution is that of maximum probability, and hence is an expression of the Maxwell-Boltzmann distribution law.

5. Introduction of a Continuous Variable.—For purposes of mathematical convenience, in order to be able to use the language of integral calculus instead of that of summations, it is sometimes desirable to change Equation 14 by the introduction of continuous variables. If we do this, we may rewrite Maxwell's distribution law in the form³

³ The symbols used in this formula were purposely chosen to agree with those used by Adams (THIS JOURNAL, 43, 1251 (1921)). The choice, however, may be somewhat misleading since the symbolism does not agree with the earlier use of Gibbs.

In Gibbs' use, the quantity $e^{\frac{\psi - \epsilon}{\theta}} dQ_1 \dots dP_m$ is the *fraction* of the total number of systems in a canonical ensemble of systems having coördinates and momenta falling in a particular infinitesimal range, and it can be shown that ψ may be taken as the Helmholtz free energy of a single system chosen from the ensemble, the average value $\bar{\epsilon}$ may be taken as sensibly equal to the energy of a single system and θ may be put proportional to the absolute temperature.

In the use adopted in this article, $e^{\frac{\psi - \epsilon}{\theta}} d\sigma$ is the *number* of molecules having coördinates and momenta falling in a particular infinitesimal range, ψ is related to the Helmholtz free energy by Equation 39,

$$N_A \psi = \left(\frac{\partial F}{\partial n} \right)_{v, T} - RT$$

the average value $\bar{\epsilon}$ is related to thermodynamic quantities by Equation 40,

$$u N_A \bar{\epsilon} = E - F + n \left(\frac{\partial F}{\partial n} \right)_{v, T} - nRT$$

and θ is again proportional to the absolute temperature.

$$dN = e^{\frac{\psi - \epsilon}{\theta}} d\sigma \quad (15)$$

where dN is the number of molecules falling in any particular infinitesimal region $d\sigma$, ψ can easily be shown by a comparison of Equations 14 and 15 to have the value $\Psi - \theta \log d\sigma$, ϵ is the rate of increase in the energy of the system per molecule introduced into the region $d\sigma$, and θ has the same value as in Equation 14.

Equation 15 is the final form in which we shall find it desirable to express the Maxwell-Boltzmann distribution law.

6. Three Important Corollaries of Maxwell's Distribution Law.—

For our further considerations we shall need some equations which may be derived as immediate consequences of Maxwell's distribution law.

For the total number of molecules we may evidently write

$$N = \int e^{\frac{\psi - \epsilon}{\theta}} d\sigma \quad (16)$$

where the integration is to be taken over the whole of the $2n$ -dimensional space σ involved.

For the average value of any property P of the molecules, which depends on their location in the generalized space σ , we may evidently write

$$P_{av.} = \frac{1}{N} \int e^{\frac{\psi - \epsilon}{\theta}} P d\sigma$$

or

$$NP_{av.} = \int e^{\frac{\psi - \epsilon}{\theta}} P d\sigma \quad (17)$$

where the integration is again to be taken over the whole of the generalized space if we desire the average value for all the molecules of the system.

For the *probability* of the configuration determined by Maxwell's distribution law, it is evident from Equation 5 that we may write

$$\begin{aligned} \log W &= N \log N - \sum N_i \log N_i \\ &= N \log N - \int e^{\frac{\psi - \epsilon}{\theta}} \log \left\{ e^{\frac{\psi - \epsilon}{\theta}} d\sigma \right\} d\sigma. \end{aligned}$$

Substituting Equation 17, and noting that $d\sigma$ has the same value in all parts of the generalized space this may easily be transformed into

$$\log W = \left(\frac{N\epsilon - N\psi}{\theta} \right)_{av.} + N \log N - N \log d\sigma \quad (18)$$

It will be noted as already pointed out by Planck that the numerical value of W depends on the size we ascribe to $d\sigma$.

III. The Thermodynamic Significance of the Quantities Occurring in Maxwell's Distribution Law.

We may now proceed to our main task of determining the thermody-

dynamic significance of the quantities occurring in the Maxwell-Boltzmann distribution law.

1. **The Analytical Nature of ϵ , ψ and θ .** Let us first recall the mathematical significance of the quantities in question.

ϵ in accordance with Equation 11

$$\partial E / \partial N_i = \epsilon_i \quad (11)$$

is the rate of change of the energy of the system per molecule added to the particular region $d\sigma$ under consideration. ϵ is obviously a function of σ since its value will depend on the coördinates and momenta corresponding to the region $d\sigma$ involved.

Attention must also be particularly called to the way in which the quantity $\partial E / \partial N_i$ first entered our discussion in Equation 8, which shows that ϵ is the rate of change of the energy of the system per molecule added to the region $d\sigma$ when the system has reached its configuration of maximum probability, with a definite number of molecules N , a definite energy content E and contained in a definite volume v . Hence ϵ for a given region $d\sigma$ may have a different value when we consider the configuration of maximum probability with different values for N , E or v . For this reason ϵ is not only a function of the variable σ but also of the parameters N , E and v . *It is believed that this discussion considerably increases the precision of our knowledge of the nature of the quantity ϵ , and will be of importance for the progress of statistical mechanical theory, particularly if we later desire to apply statistical mechanical methods to a study of imperfect gases or other concentrated systems.*

ψ and θ are dependent as already shown, in a simple manner on the undetermined multipliers λ and μ which were introduced when the equations restricting the variation in number of molecules and in energy were combined with the general equation for variation in probability. It is evident from the method of introduction that ψ and θ are independent of σ and are dependent only on the whole state of the system. They will in general, therefore, be functions of the parameters N , E and v .

2. **The Thermodynamic Significance of θ .**—As to the thermodynamic significance of θ , it is well known that this quantity is related to the absolute temperature of the system T by the equation

$$\theta = kT \quad (19)$$

where k is the gas constant R divided by Avogadro's number.

The proof of this relation consists in showing that two systems of molecules which are allowed to interact will have the same value of θ , and then showing that if one of these systems is an ideal gas consisting of non-attracting point particles, the value of θ for that system is given by the equation $\theta = pv/N$ where p , v and N are the pressure, volume and number

of molecules of the gas. As the proof is simple and well known⁴ but somewhat long, it does not seem desirable to repeat it here, since we are more particularly interested in the thermodynamic significance of ψ and ϵ concerning which there has been some doubt.

3. The Expression for Entropy.—In order to show the thermodynamic significance of ψ and ϵ we shall obtain an expression for the entropy of the system which is dependent on these quantities.

Except for an additive constant, in which we are not now interested, the entropy of a *homogeneous* system can be completely defined by the thermodynamic equations

$$\left(\frac{\partial S}{\partial E}\right)_{v,N} = \frac{1}{T} \quad (20)$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T} \quad (21)$$

$$\left(\frac{\partial S}{\partial N}\right)_{p,T} = \frac{S}{N} \quad (22)$$

The first two of these equations are direct consequences of the fundamental equation

$$dS = \frac{dE + p dv}{T}$$

and the third equation results from the fact that the entropy of a system is always taken as the sum of the entropies of its parts, and hence for a *homogeneous* system, which has the same pressure and temperature throughout, the entropy of any part will be proportional to the number of molecules in the part taken.

The problem, now before us, is to find a statistical mechanical quantity which has the differential coefficients given by Equations 20, 21 and 22. We shall find that a solution of this problem is given by the equation

$$S = k \left(\frac{N\bar{\epsilon} - N\psi}{\theta} \right)_{\text{av.}} \quad (23)$$

Substituting Equation 19, denoting the average value of ϵ by the symbol $\bar{\epsilon}$, and noting in accordance with our previous discussion that since ψ is independent of σ , it and its average value are the same, we may rewrite the above in the form

$$S = \frac{N\bar{\epsilon} - N\psi}{T} \quad (24)$$

Let us now show that the quantity given by Equation (24) actually does obey Equations 20, 21 and 22. To do this we must first obtain a mathematical identity which we shall need in the discussion.

⁴ See for example, Tolman, *Phil. Mag.*, **28**, 583 (1914) or "The Theory of the Relativity of Motion," Chapter VIII, "The Chaotic Motion of a System of Particles," University of California Press, 1917.

In accordance with Maxwell's distribution law we may write

$$N = \int e^{\frac{\psi - \epsilon}{kT}} d\sigma$$

Differentiating with respect to the parameter E , keeping the other two parameters v , and N constant,⁵ we obtain

$$0 = \left(\frac{\partial N}{\partial E} \right)_{v,N} = \int \frac{\partial}{\partial E} \left(e^{\frac{\psi - \epsilon}{kT}} \right) d\sigma = \int e^{\frac{\psi - \epsilon}{kT}} \frac{\partial}{\partial E} \left(\frac{\psi - \epsilon}{kT} \right) d\sigma \quad (25)$$

We may now determine the derivative of $\frac{N\bar{\epsilon} - N\psi}{T}$ with respect to energy. Noting Equation 17 for the average value of a quantity, we may write.

$$\begin{aligned} \left(\frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{T} \right)_{v,N} &= \frac{\partial}{\partial E} \int e^{\frac{\psi - \epsilon}{kT}} \frac{\epsilon - \psi}{T} d\sigma \\ &= \int \frac{\partial}{\partial E} \left(e^{\frac{\psi - \epsilon}{kT}} \right) \frac{\epsilon - \psi}{T} d\sigma + \int e^{\frac{\psi - \epsilon}{kT}} \frac{\partial}{\partial E} \left(\frac{\epsilon - \psi}{T} \right) d\sigma \end{aligned}$$

Remembering that ψ and T are independent of σ , this may be rewritten in the form

$$\begin{aligned} \left(\frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{T} \right)_{v,N} &= \frac{1}{T} \int \frac{\partial}{\partial E} \left(e^{\frac{\psi - \epsilon}{kT}} \right) \epsilon d\sigma - \frac{\psi}{T} \int \frac{\partial}{\partial E} \left(e^{\frac{\psi - \epsilon}{kT}} \right) d\sigma + \int e^{\frac{\psi - \epsilon}{kT}} \frac{\partial}{\partial E} \left(\frac{\epsilon - \psi}{T} \right) d\sigma. \end{aligned}$$

In accordance with Equation 25, it is evident, however, that the last two terms in this equation are zero. As to the first term on the right hand side of the above equation, it is evident that the quantity $\frac{\partial}{\partial E} \left(e^{\frac{\psi - \epsilon}{kT}} \right)$ is the rate of change in the number of molecules in region $d\sigma$ with change in E , while ϵ is the rate in change of the energy per molecule added to the region $d\sigma$. Hence the value of the definite integral is evidently $\partial E / \partial E = 1$. Our expression thus reduces to

$$\left(\frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{T} \right)_{v,N} = \frac{1}{T} \quad (26)$$

thus agreeing with the first of the three necessary equations (20), (21) and (22).

Let us now proceed to show that the rate of change of $\frac{N\bar{\epsilon} - N\psi}{T}$ with respect to volume has the required value.

⁵ It should be noted that the constancy of v makes it possible to differentiate solely back of the integral sign, since under these circumstances the limits of integration are constant.

In our previous discussions we have made use of the principle that an isolated system, with a definite energy content E in a container of definite volume v , will assume the statistical state of maximum probability. For our present purposes, we shall make use of the equally valid principle, that the system will assume the statistical state of maximum probability when it is enclosed in a cylinder with walls which do not permit the transfer of energy and provided with a movable piston, thus allowing a simultaneous variation in the parameters E and v , in accordance with the equation

$$\delta E = -p \delta v. \quad (27)$$

Now we have already found, in accordance with Equation 18, that when the parameters E and v are not allowed to vary, the probability W of the state finally attained is given by the expression

$$\log W = \left(\frac{N\bar{\epsilon} - N\psi}{kT} \right) + N \log N - N \log d\sigma. \quad (28)$$

The variation in this quantity with the parameters E and v will evidently be

$$\delta \log W = \left(\frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{kT} \right)_{v, N} \delta E + \left(\frac{\partial}{\partial v} \frac{N\bar{\epsilon} - N\psi}{kT} \right)_{E, N} \delta v$$

In the special case that we are considering, W has the maximum possible value not only for changes in internal arrangement with constant values of E and v but also for variations in E and v which do not conflict with the restriction imposed by Equation 27. Hence by introducing Equation 27 and applying the condition for maximum probability, we obtain

$$-\left(\frac{\partial}{\partial E} \frac{N\bar{\epsilon} - N\psi}{kT} \right)_{v, N} p \delta v + \left(\frac{\partial}{\partial v} \frac{N\bar{\epsilon} - N\psi}{kT} \right)_{E, N} \delta v = 0$$

Multiplying by k , dividing by δv , and introducing the expression we have already found for the rate of change of $\frac{N\bar{\epsilon} - N\psi}{T}$ with E , we obtain and

$$\left(\frac{\partial}{\partial v} \frac{N\bar{\epsilon} - N\psi}{T} \right)_{E, N} = \frac{p}{T} \quad (29)$$

have thus shown the desired agreement with the second of our three necessary equations (20), (21) and (22).

In order to show the agreement of the quantity that we have chosen for entropy with the third of the three equations, we shall first need to obtain an auxiliary equation by differentiating the expression for Maxwell's distribution law

$$N = \int e^{\frac{\psi - \epsilon}{kT}} d\sigma$$

with respect to the number of molecules N , holding the pressure p and temperature T constant. In carrying out such a differentiation, it is to

be noted that we cannot consider the limits of the definite integral as constant, since the volume v of a homogeneous system at a given pressure and temperature is evidently proportional to the number of molecules N , and the volume over which the generalized space $d\sigma$ is to be integrated is proportional to v . Keeping this consideration in mind, we may write

$$\left(\frac{\partial N}{\partial N}\right)_{p, T} = \int \frac{\partial}{\partial N} \left(e^{\frac{\psi - \epsilon}{kT}} \right) d\sigma + \left(e^{\frac{\psi - \epsilon}{kT}} \right)_{lim} \frac{\partial \sigma_{lim}}{\partial N}.$$

Noting further that the last term in this equation is evidently itself equal to $\partial N / \partial N$, and that $\partial \bar{\epsilon} / \partial N$ is obviously zero since we have in no way changed the condition inside of any given region $d\sigma$, we obtain

$$0 = \int e^{\frac{\psi - \epsilon}{kT}} \frac{1}{kT} \frac{\partial \psi}{\partial N} d\sigma$$

or remembering that ψ and its average value for the system are the same, we may write

$$\left(\frac{\partial \psi}{\partial N}\right)_{p, T} = 0 \quad (30)$$

We may now differentiate our expression for entropy with respect to N . We obtain

$$\left(\frac{\partial}{\partial N} \frac{N\bar{\epsilon} - N\psi}{T}\right)_{p, T} = \frac{\bar{\epsilon} - \psi}{T} + \frac{N}{T} \frac{\partial \bar{\epsilon}}{\partial N} - \frac{N}{T} \frac{\partial \psi}{\partial N},$$

We have just shown, however, that the last term in this equation is equal to zero, and it is evident, moreover, that $\partial \bar{\epsilon} / \partial N$ is zero, since with constant pressure and temperature the value of ϵ for every region $d\sigma$ remains unchanged. Hence we may rewrite the above equation in the form

$$\left(\frac{\partial}{\partial N} \frac{N\bar{\epsilon} - N\psi}{T}\right)_{p, T} = \frac{1}{N} \left(\frac{N\bar{\epsilon} - N\psi}{T}\right). \quad (31)$$

We have thus shown the agreement of the expression which we have chosen for entropy with the third and last of the three necessary equations (20), (21) and (22), and may now write

$$S = \frac{N\bar{\epsilon} - N\psi}{T}$$

or if desired

$$S = \frac{N\bar{\epsilon} - N\psi}{T} + N \times \text{const.} \quad (32)$$

4. Other Equations Connecting Statistical Mechanics and Thermodynamics.—Equation 32 shows perhaps as well as any, the thermodynamic significance of the statistical mechanical quantities ϵ and ψ . A number of other equations interrelating the two methods of attack, however, will also be of interest.

Differentiating the expression for Maxwell's distribution law at constant volume and temperature we obtain

$$\begin{aligned} \left(\frac{\partial N}{\partial N}\right)_{v,T} &= 1 = \int \frac{\partial}{\partial N} \left(e^{\frac{\psi-\epsilon}{kT}} \right) d\sigma \\ &= \int e^{\frac{\psi-\epsilon}{kT}} \frac{1}{kT} \frac{\partial \psi}{\partial N} d\sigma - \int e^{\frac{\psi-\epsilon}{kT}} \frac{1}{kT} \frac{\partial \epsilon}{\partial N} d\sigma \\ \text{or } kT &= \int e^{\frac{\psi-\epsilon}{kT}} \frac{\partial \psi}{\partial N} d\sigma - \frac{\partial}{\partial N} \int e^{\frac{\psi-\epsilon}{kT}} \epsilon d\sigma + \int \frac{\partial}{\partial N} \left(e^{\frac{\psi-\epsilon}{kT}} \right) \epsilon d\sigma \end{aligned}$$

An inspection of the last term of this equation shows that it is equal to $\partial E/\partial N$. Introducing Equation 17 for the average value of a quantity, remembering the relation between ψ and its average value, and solving for $\partial E/\partial N$, we obtain,

$$\left(\frac{\partial E}{\partial N}\right)_{v,T} = \bar{\epsilon} + N \left(\frac{\partial \bar{\epsilon}}{\partial N}\right)_{v,T} - N \left(\frac{\partial \psi}{\partial N}\right)_{v,T} + kT. \quad (33)$$

This is an equation of some interest, owing to the thermodynamic importance of the quantity $\partial E/\partial N$.

Another thermodynamic quantity of importance is the Helmholtz free energy which may be defined by the equation

$$F = E - TS. \quad (34)$$

Introducing the expression for entropy given by Equation 32, we have,

$$F = N\psi - N\bar{\epsilon} + E. \quad (35)$$

an equation which reduces to

$$F = N\psi \quad (36)$$

for the special case of a perfect gas.

The derivative of F with respect to N , at constant volume and temperature is also of interest. We have

$$\left(\frac{\partial F}{\partial N}\right)_{v,T} = \psi + N \left(\frac{\partial \psi}{\partial N}\right)_{v,T} - \bar{\epsilon} - N \left(\frac{\partial \bar{\epsilon}}{\partial N}\right)_{v,T} + \left(\frac{\partial E}{\partial N}\right)_{v,T}$$

which, on substitution of Equation 33, becomes

$$\left(\frac{\partial F}{\partial N}\right)_{v,T} = \psi + kT \quad (37)$$

or putting

$$N = n N_A \quad (38)$$

where n is the number of mols in the system and N_A is Avogadro's number, Equation 37 becomes

$$\left(\frac{\partial F}{\partial n}\right)_{v,T} = N_A \psi + kT \quad (39)$$

or

$$N_A \psi = \left(\frac{\partial E}{\partial n}\right)_{v,T} - kT.$$

This equation shows in a very simple way the thermodynamic significance of ψ , since except for ψ it contains none but thermodynamic quantities.

A similar equation containing ϵ and none but thermodynamic quantities is, of course, impossible since it is the average value of ϵ rather than its value for any particular region $d\sigma$ that has thermodynamic significance. An equation containing the average value $\bar{\epsilon}$ and none but thermodynamic quantities can be obtained by substituting (38) and (39) in our expression for entropy Equation 32, we obtain

$$n N_A \bar{\epsilon} = E - F + n \left(\frac{\partial F}{\partial n} \right)_{v,T} - nkT \quad (40)$$

which can be shown to reduce to

$$n N_A \bar{\epsilon} = E \quad (41)$$

for the special case of a perfect gas.

IV. Comparison with Results of Planck.

In conclusion it will be of interest to compare the expression which we have obtained for the entropy of a system with that of Planck.⁶

Planck defines entropy by the equation

$$S = k \log W \quad (42)$$

where W is the probability of the configuration. We, on the other hand, have taken the quantity

$$S = \frac{N^* - N\psi}{T} \quad (43)$$

as entropy, since it has the same derivatives with respect to energy, volume, and number of molecules as does entropy.

In order to compare our equation with that of Planck, we may introduce into (43) the expression which we obtained for probability, as given by Equation 18. We obtain

$$S = k \log W - kN \log N + kN \log d\sigma. \quad (44)$$

It is apparent that our expression for entropy and that of Planck differ from each other in an important manner, and that this difference is not merely due to the fact that in accordance with the classical statistical mechanics we have divided our generalized space σ into infinitesimal regions of equal size $d\sigma$, while Planck in accordance with his form of quantum theory divides the space σ into regions of finite size G .

Both our expression for entropy and Planck's have the same derivatives with respect to energy and volume, but different derivatives with respect to the number of molecules N . This is a fundamental difference between the expressions and the reason why Planck's expression for entropy is not satisfactory when considerations are to be undertaken which involve a change in the number of elements.

⁶ The difficulties involved in defining entropy by the equation $S = k \log W$ and at the same time making the entropy of a system equal to the sum of the entropies of its parts have also been pointed out by Mrs. T. Ehrenfest-Afanassjewa, *Verslag. Akad. Wetenschappen Amsterdam*, 21, 53 (1919).

In order to make this point entirely clear, let us take Planck's expression for entropy using finite regions and summations as he does.

The Planck expression for entropy may be written

$$S = k \log W = kN \log N - k \sum_{i=1,2,3,\dots,m} N_i \log N_i \quad (45)$$

where the summation is to be carried out over all the regions $i=1,2,3,\dots,m$ that contain molecules.

Consider the change in this quantity corresponding to a change δN in the number of molecules, pressure and temperature being maintained constant. For a *homogeneous* system it is evident that the number of molecules falling in any particular region will not be changed provided temperature and pressure are maintained constant. Hence we may write

$$(\delta S)_{p,T} = k (\log N + 1) \delta N - k \sum_{i=(m+1)(m+2)\dots(m+\delta m)} N_i \log N_i \quad (46)$$

where the summation is carried out over the new regions $(m+1)(m+2)\dots(m+\delta m)$ which have been created by the increase in volume which accompanies the increase in number of molecules.

Owing to the similarity of the distribution in the new regions to that in the old, it is evident that we may rewrite the last term in the form

$$k \sum_{i=(m+1)(m+2)\dots(m+\delta m)} N_i \log N_i = \left\{ k \sum_{i=1,2,3,\dots,m} N_i \log N_i \right\} \frac{\delta N}{N} \quad (47)$$

Substituting (6) and dividing by δN we obtain

$$\left(\frac{\delta S}{\delta N} \right)_{p,T} = k \log N - \frac{k}{N} \sum N_i \log N_i + k. \quad (48)$$

We note that $\left(\frac{\delta S}{\delta N} \right)_{p,T}$ is not equal to S/N as is required for a successful definition of entropy.

For a successful definition along the Planck lines we might suggest

$$S = k \log W - kN \log N. \quad (49)$$

This expression would make the entropy of a system at constant pressure and temperature proportional as it should be to the total number of molecules present. It would also make the absolute numerical value of S depend on the finite size G , which Planck chooses for his regions of equal probability, in the way that Planck desires. It should further be pointed out that there is no disagreement between Equation 49 and our own Expression 44 since we have already called attention to the fact (see Equation 32) that it is allowable to add to our expression for entropy any desired constant multiplied by N .

Summary.

1. The relation between statistical mechanics and thermodynamics has been investigated in this article by a method which is based like that

of Boltzmann and Planck on a consideration of the arrangement of the elements or molecules of a system. Instead, however, of following the procedure of Boltzmann and Planck by somewhat arbitrarily defining entropy by the equation

$$S = k \log W$$

the attempt has been made in this article to discover a statistical mechanical quantity which has the same derivatives with respect to energy, volume and number of molecules as does the thermodynamic quantity entropy. In this way we have been led to an expression for entropy which differs from that of Planck by an additive term, and have shown that the addition of such a term is, as a matter of fact, necessary in order that the derivative of the entropy of the system with respect to number of molecules shall have its correct value.

2. In connection with the derivation, it has been shown that the quantity E occurring in the Maxwell-Boltzmann distribution law

$$dN = C e^{-\frac{\epsilon}{kT}} dq_1 \dots dp_n$$

must be taken, *not* as the energy of a molecule having coördinates and momenta falling in the region $dq_1 \dots dp_n$, but *rather* as the rate of increase in the total energy of the system per molecule added to the region $dq_1 \dots dp_n$, when the system is in its configuration of maximum probability. These two quantities are the same for dilute gases, but for concentrated systems may be quite different. Hence the new methods which are introduced may be of considerable importance in dealing with the properties of imperfect gases or rather concentrated systems.

3. It was pointed out that the equations obtained in this article connecting the statistical mechanical quantities occurring in the Maxwell-Boltzmann distribution law with thermodynamic quantities, do not agree with the equations of Marcelin and Adams.²

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]
THE DISTRIBUTION OF THERMAL ENERGY IN THE TETRACHLORIDES OF CARBON, SILICON, TITANIUM AND TIN.

BY WENDELL M. LATIMER.

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The determination of the specific heats and heats of fusion of several tetrachlorides of the fourth periodic group was undertaken in connection with the study of the effect of mass upon the distribution of thermal energy. When the conditions in a solid are such that the thermal energy is distributed according to the principle of the equipartition of energy, the specific heat per gram atom is independent of the mass; however, when the "equipartition conditions" are not fulfilled, whatever the exact nature of