Physics. — *"Entropy and Probability."* By Dr. L. S. Ornstein. (Communicated by Prof. Lorentz).

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Einstein [1]) has defined the probability of state in a way by which he emancipates himself from special hypotheses concerning the structure of the systems to which he applies his reasonings. He puts the logarithm of the probability thus defined proportional to the entropy. If therefore $d\varepsilon$ is the difference of energy between two states of the system, and if dA represents the work done by the system if it passes in a reversible way from one state into the other we have

$$d\eta = \frac{R}{N} d \log W = \frac{d\varepsilon + dA}{T},$$

R is the gas constant and N the number of molecules of the gramme-molecule. The reasoning, used to deduce the proportionality of η and $\frac{R}{N} \log W$, is perhaps not quite convincing, for on the one side it is presumed that a system runs through all states possible with the given energy, and on the other that $\log W$ like the entropy tends to a maximum value. It is possible by means of statistical mechanics (as well with the help of the canonical as with that of the micro-canonical ensembles) to find the relation of entropy and probability, however using many less general hypotheses as those employed by Einstein. I will try to show this in the following communication.

1. We consider a system of a great number (s) of degrees of liberty. We suppose that the changes of the state in this system are governed by the equations of Hamilton. Observation does not teach us anything on the s general coordinates (q) and the s moments of momentum (p) but we obtain knowledge of certain (e. g. geometrical) quantities A. Suppose that there are k quantities A_k which are discernable for observation. The number k is small in comparison to $2s$. We shall indicate these quantities by $A_1 .. A_\nu .. A_k$ [2]).

To the $2s$ values of the coordinates and the moments in a given

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[1]) Ann. der Phys Vol 33, 1910, p. 1276.

[2]) The quantities A may be geometrical quantities but also densities in given spaces. The quantities determining deformation must be used in several cases, also the optical qualities of the system, in other cases we have to do with thermical quantities relating to parts of the system accessible to observation, and which may be said to characterise the system for it.

state of the system corresponds a perfectly determined set of values A, on the contrary it must be kept in mind that a great number of systems with greatly differing values for the p's and the q's corresponds to a given set of values of the A_r's.

Moreover we must presume that the quantities A_r are observable with moderate accuracy, so that systems for which A_x has a value between A_x and $A_x + dA_r$ are undiscernible for observation. The quantities ΔA are once for all fixed (in relation to the given accuracy of observation); ΔA_r will be small compared with A_x.

A system having its A_r's between the limits mentioned will be called the system $(A_1 .. A_r .. A_k)$. For the sake of simplicity we shall suppose that the quantities A_r depend only on the general coordinates [1]).

The $2s$-dimensional space in which the system can be represented in the ordinary way can be dissolved into the extension in configuration, (the coordinates being the variables) and into the extension in moments or velocity. The part of the extension in configuration where the systems lie for which the value of the A_r is between A_r and $A_r + dA_r$ will be represented by

$$\chi(A_1 .. A_r .. A_k) \, dA_1 .. dA_r .. dA_k$$

or shortly by

$$\chi dA_1 .. dA_r .. dA_k .$$

We shall further suppose that the potential energy ε_q of the system of given A_r's is totally determined by the values of the quantities A_x. This is only approximately true, for ε_q depends on the coordinates, which can still be greatly different for systems of which the A_r's are the same. We shall represent the potential energy by

$$\varepsilon_q(A_1 .. A_r .. A_k, a_1 . . a_n),$$

the quantities a denoting parameters on which the potential energy may also depend; the same parameters shall appear generally also in the function χ.

Finally we could suppose that there exist relations between the quantities A_r, suppose for example b $(b < k)$ of the form

$$f_\beta = 0.$$

For such a case we can always introduce $k-b$ new quantities A which are mutually independent, we therefore shall suppose that this is yet the case for the A_r's mentioned above [2]).

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[1]) It is however not difficult to extend the considerations to those cases where this is not so and where the Λ_x can be thermical quantities.

[2]) This need not be the case if we take as variables such quantities which are suggested by the nature of the problem, e. g. there exists a relation between the

2. We shall now consider a microcanonical ensemble between the energies ε and $\varepsilon + d\varepsilon$, consisting of the systems described above. I shall represent the part of the extension in configuration for which the quantities A_r are situated between the limits A_r and $A_r - dA_r$ by $\Omega(A_1 \cdot A_r \ldots A_k)$. The value of Ω may be expressed by the equation.

$$\Omega(A_1 \cdot .A_r \ldots A_k) = C \{(\varepsilon - \varepsilon_q (A_1 \cdot .A_r \cdot . A_k)\}^{\frac{s}{2}-1}$$

$$\chi \cdot dA_1 \cdot . dA_r \cdot . dA_k \, d\varepsilon ;$$

C being a determined numerical constant which is of no importance to us. The quantities A_r must have such values that $\varepsilon_q \leq \varepsilon$.

We shall first consider the question for which values of A_r, Ω is a maximum, i.e. which values of the A_r occur in a maximal region.

We find for the maximum condition, proceeding in the usual way,

$$-\left(\frac{s}{2} - 1\right)\frac{1}{\varepsilon - \varepsilon_q (A_1 \cdot . A_r \cdot . A_k)}\frac{\partial \varepsilon_q}{\partial A_r} + \frac{1}{\chi}\frac{\partial \chi}{\partial A_r} = 0.$$

The quantity $\varepsilon - \varepsilon_q (A_r)$ being the kinetic energy of the system occurring maximally, this quantity is, as is proved by GIBBS, proportional to the absolute temperature T and it can be expressed by the formula

$$\frac{s}{2}\frac{R}{N} T.$$

Neglecting 1 with respect to $\frac{s}{2}$, s being very large, we find as a condition for the maximum of Ω

$$-\frac{N}{RT}\frac{\partial \varepsilon_q}{\partial A_k} + \frac{1}{\chi}\frac{\partial \chi}{\partial A_k} = 0.$$

The further conditions that $d^2 \log \Omega < 0$ lead to a number of relations of the form:

$$-\frac{s-2}{2}\frac{1}{\varepsilon_p^2}\left(\frac{d\varepsilon_q}{\partial A_r}\right)^2 - \frac{s-2}{2\varepsilon_p}\frac{d^2\varepsilon_q}{\partial A_r^2}$$

$$-\frac{1}{\chi^2}\left(\frac{d\chi}{\partial A_r}\right)^2 + \frac{1}{\chi}\frac{d^2\chi}{\partial A_r^2} < 0,$$

and to a number of relations in which the quantities $\dfrac{d^2}{\partial A_r \partial A_\mu}$

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densities in fixed elements of volume in a gas. In practice one will not use the relations to eliminate the A_r but will use the Laplacian method of undetermined coefficients. It is also possible that inequalities appear as relations in every case; it follows from our first hypothesis that we may assume that the relations are fulfilled without any approximation.

play a part. The complication offered by the appearance of these quantities may always be avoided by a linear substitution which removes those differential coefficients. I shall suppose that such-like A_x's are introduced (further representing them by the same symbol A_ν); A_{ν_0} represents the value of A_k in the maximum system.

3. The region Ω where those systems are represented for which A_x is situated between $A_{\nu_0} + \xi_\nu$ and $A_{\nu_0} + \xi_\nu + d\xi_\nu$ can be easily calculated; we find for it:

$$\Omega_\Delta = \Omega_0 e^{\frac{1}{2}\sum_1^k p_\nu \xi_\nu{}^2} d\xi_1 \ldots d\xi_\nu \ldots d\xi_k d\varepsilon$$

where

$$\Omega_0 = C\chi\,(A_{10} \ldots A_{\nu_0} \ldots A_{k_0})\,(\varepsilon - \varepsilon_q)^{\frac{s}{2}-1}$$

and

$$p_\nu = -\frac{N}{RT\varepsilon_{p_0}}\left(\frac{\partial\varepsilon_q}{\partial A_\nu}\right)^2 - \frac{N}{RT}\frac{\partial^2\varepsilon_q}{\partial A_\nu{}^2} - \frac{1}{\chi^2}\left(\frac{\partial\chi}{\partial A_\nu}\right)^2 + \frac{1}{\chi}\frac{\partial^2\chi}{\partial A_\nu{}^2}.$$

The expression found above can be used to calculate the total volume of the extension in phase of the space where the energy is contained between the given limits. For this purpose we have to take the sum of Ω_Δ for all the values of A_ν's which are compatible with the given energy. However, we can integrate with respect to the ξ_ν from $-\infty$ to $+\infty$, the values of ξ_ν which deviate considerably from 0, attributing only very small amounts. Proceeding in this way we find for the extension in question, which we shall represent by the notation of Gibbs $e^{\eta}d\varepsilon$ or $\dfrac{\partial V}{\partial\varepsilon}d\varepsilon$

$$\frac{\partial V}{\partial\varepsilon}d\varepsilon = e^{\eta}d\varepsilon = \frac{C\Omega_0}{(p_1 \ldots p_\nu \ldots p_k)^{1/2}}d\varepsilon,$$

C being again a determined constant, the value of which is without importance for our conclusions.

With the help of the found expression we can express the value of the function $V(\varepsilon)$ which determines the magnitude of the part of the extension in phase for which the energy of the represented systems is smaller than ε.

We obtain for $V(\varepsilon)$ the expression

$$V = C'\int_{\varepsilon\,(V=0)}^{\varepsilon}\frac{\chi\,(A_{10} \ldots A_{\nu_0} \ldots A_{k_0})}{\sqrt{(p_1 \ldots p_x \ldots p_\nu)}}\,(\varepsilon - \varepsilon_q\,(A_1 \ldots A_{\nu_0} \ldots A_k))^{\frac{s}{2}-1}d\varepsilon\ .$$

The value of the integral can easily be obtained in case that the

value of the A_r, for which Ω is a maximum, is independent of ε. Then we may assume $\varepsilon(V=0) = \varepsilon_q (A_{1_0}. A_{r_0}..A_{k_0})$. Substituting this value we find

$$V = C' \frac{\chi(A_{1_0}. A_{x_0}.A_{k_0})}{\sqrt{(p_1 ... p_{r..}. p_k)}} \frac{2}{s} (\varepsilon - \varepsilon_q (A_{1_0}..A_{r_0}..A_{k_0})^{\frac{s}{2}}.$$

But the same relation holds for other cases. The quantity A_{r_0} depending on ε, we have

$$\frac{V}{c} = \int_{\varepsilon(V=0)}^{\varepsilon} (\varepsilon - \varepsilon_q(A_{1_0}.. A_{r_0}. A_{k_0})^{\frac{s}{2}-1} \chi(A_{1_0}.. A_{r_0}..A_{k_0})\, d\varepsilon$$

$$= \frac{2}{s} (\varepsilon - \varepsilon_q (..A_{r_0}..))^{\frac{s}{2}} \chi(A_{r_0}) \Big|_{\varepsilon(V=0)}^{\varepsilon} + \int_{\varepsilon(V=0)}^{\varepsilon} (\varepsilon - \varepsilon_q(..A_{r_0}))^{\frac{s}{2}-1} \chi(..A_{r..})$$

$$\sum_1^k \left\{ \frac{\partial \varepsilon_q}{\partial A_{r_0}} \frac{\partial A_{r_0}}{\partial \varepsilon} \right\} d\varepsilon$$

$$- \frac{2}{s} \int_{\varepsilon(V=0)}^{\varepsilon} (\varepsilon - \varepsilon_q (A_{r_0}))^{\frac{s}{2}-1} \sum_1^k \frac{\partial \chi}{\partial A_{x_0}} \frac{\partial A_{x_0}}{\partial \varepsilon}\, d\varepsilon.$$

Combining the integrals we find

$$\frac{2}{s} \int_{\varepsilon(V=0)}^{\varepsilon} (\varepsilon - \varepsilon_q(A_{r_0}))^{\frac{s}{2}} \chi(A_{r_0}) \left\{ \sum_1^k \left(\frac{s}{2(\varepsilon - \varepsilon_{q_0})} \frac{\partial \varepsilon_q}{\partial A_r} - \frac{1}{\chi} \frac{\partial \chi}{\partial A_{r_0}} \right) \frac{\partial A_{r_0}}{\partial \varepsilon} \right\} d\varepsilon.$$

Every term of the integrals is zero. The kinetic energy being essentially positive we have at the limit $\varepsilon(V=0)\, \varepsilon = \varepsilon_q$, so that we obtain

$$V = \frac{2}{s} C (\varepsilon - \varepsilon_q (A_{r_0}))^{\frac{s}{2}} \chi(A_{x_0})$$

A_{r_0} having the value relating to the energy ε.

In this demonstration Vp_r has been neglected, the influence however of these factors is small, they deviate only very slightly from 1, if compared with the quantities taken into consideration.

4. GIBBS has proved that *log V* is equivalent with the thermodynamic entropy. If two microcanonical ensembles whose energy differs $\Delta \varepsilon$ and whose parameters differ by Δa there exists an equation of the form

$$e^{-\varphi} \; V \; \Delta \; log \; V = \Delta \varepsilon + \overline{A} \big|_{\varepsilon} \Delta a \; ^1) \quad . \quad . \quad . \quad . \quad (I)$$

in this equation $\overline{A}\big|_{\varepsilon}$ is the average force in the ensemble exercised with

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[1]) For the case under consideration we can prove without applying the general discussions of GIBBS that $\frac{\varepsilon p}{2s}$ shows a perfect analogy with the temperature, and the relation (I) can be proved somewhat more simply than it has been done by GIBBS.

Let us imagine two systems of the kind described above, which can interchange energy but which considered as a whole are isolated. Let us suppose that the first has s_1, the second s_2 degrees of freedom, the energy of the first being ε_1, that of the second ε_2. The total energy being constant we have

$$\varepsilon_1 + \varepsilon_2 = \varepsilon.$$

The quantity φ_{12} of the combined system can be expressed (GIBBS l.c. p. 98 form. 316) by

$$e^{\varphi_{12}} = \int e^{\varphi_1 + \varphi_2} \, d\varepsilon_2.$$

If we represent the value of (Λ_ν) when the Λ_ν have their maximum value by $\chi(\Lambda_{\nu_0})$, and if we distinguish for the first system $\varkappa$ parameters Λ_ν, and for the second n parameters λ_ν, we obtain

$$e^{\varphi_{12}} = \int (\varepsilon_1 - \varepsilon_{q_1})^{\frac{s_1}{2}-1} \chi_1(\Lambda_\nu \varepsilon_1)(\varepsilon_1 - \varepsilon_{q_2})^{\frac{s_2}{2}-1} \cdot$$
$$\chi_2(\lambda_\nu \varepsilon_2) \, d\varepsilon_2.$$

The maximum system will contribute a maximal amount to the integral. We can find this system asking for what values of ε_1 and ε_2 the function under the integral is a maximum $\varepsilon_1 + \varepsilon_2$ being a constant. We then find

$$\left(\frac{s_1}{2} - 1\right) \frac{1}{\varepsilon_1 - \varepsilon_{q_1}} \, d\varepsilon_1 + \left(\frac{s_2}{2} - 1\right) \frac{1}{\varepsilon_2 - \varepsilon_{q_2}} \, d\varepsilon_2 +$$

$$\sum_1^k \left(-\left(\frac{s_1}{2} - 1\right) \frac{\partial \varepsilon_{q_1}}{\partial \Lambda_{k_0}} + \frac{1}{\chi_1} \frac{\partial \chi_1}{\partial \Lambda_{k_0}}\right) \frac{d\Lambda_{k_0}}{d\varepsilon_1} \, d\varepsilon_1 +$$

$$\sum_1^n \left(-\left(\frac{s_2}{2} - 1\right) \frac{d\varepsilon_{q_0}}{\partial \lambda_{\nu_0}} + \frac{1}{\chi_2} \frac{d\chi_2}{\partial \lambda_{\nu_0}}\right) \frac{\partial \lambda_{\nu_0}}{\partial \varepsilon_2} \, d\varepsilon_2.$$

From the above considerations it follows that the summations in this equation are zero, the Λ_ν being the values for the most frequent forms of the separate systems. We therefore find for the systems occurring maximally

$$\frac{s_1 - 2}{2(\varepsilon_1 - \varepsilon_{q_1})} = \frac{s_2 - 2}{2(\varepsilon_2 - \varepsilon_{q_2})} = \mu$$

or

$$\frac{\varepsilon p_1}{s_1} = \frac{\varepsilon p_2}{s_2}$$

i. e. that system is most frequent for which the kinetic energies of the composing systems are proportionate to the number of degrees of freedom.

If we separate the systems, their contents of kinetic energy will fulfill with

respect to the parameter a. GIBBS has shown that $e^{-\gamma} V$ corresponds with temperature. With the help of the given relations we can cal-

great probability the theorem of equipartition. Also two systems the energies of which are proportionate to their number of degrees of freedom will be, after that communication of energy has been made possible, in a probable state and it is therefore almost certain that one system will not give or obtain energy from the other. If two systems are brought into contact whose energies are in another proportion, their state is improbable and the total system will probably change in such a way that the system for which $\dfrac{\varepsilon_p}{s}$ is too great, loses energy. What has been said is sufficient to show that $\dfrac{\varepsilon_p}{s}$ can be used as a measure for the temperature.

We have next to consider the mean force in a micro-canonical ensemble. I will give a somewhat simpler deduction than that of GIBBS.. (HERTZ has also given another treatment).

Consider an ensemble for which the density ρ in phase is a function of ε, the function $\rho(\varepsilon)$ being zero everywhere except between narrow limits in the proximity of ε_0; between the limits $\rho(\varepsilon)$ shall be supposed everywhere positive. Suppose that ε_1 and ε_2 are values of ε lying outside this region but so, that $\varepsilon_1 < \varepsilon_0 < \varepsilon_2$; we have identically

$$\int_{\varepsilon_1}^{\varepsilon^2} \varrho \, dp_1 \dots dq_s = \int_{\varepsilon_1}^{\varepsilon_2} \varrho \, e^{\varphi} \, d\varepsilon.$$

Differentiating with respect to the parameters a we obtain

$$\int_{\varepsilon_1}^{\varepsilon_2} \frac{\partial \varrho}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial a} \, dp_1 \dots dq_s = +\int_{\varepsilon_1}^{\varepsilon_2} \varrho \frac{\partial \varphi}{\partial a} e^{\varphi} \, d\varepsilon = -\int_{\varepsilon_1}^{\varepsilon_2} \frac{\partial \varrho}{\partial \varepsilon} A \, dp_1 \dots dq_s =$$

$$= -\int_{\varepsilon_1}^{\varepsilon_2} \frac{\partial \varrho}{\partial \varepsilon} \overline{A]}_{\varepsilon} \, e^{\varphi} \, d\varepsilon = \int_{\varepsilon_1}^{\varepsilon_2} \varrho \left(\frac{\partial A_{\varepsilon}}{\partial \varepsilon} e^{\varphi} + A_{\varepsilon} \frac{\partial \varphi}{\partial \varepsilon} e^{\varphi} \right) d\varepsilon.$$

The transformation on the second line follows directly from the signification of $\overline{A]}_{\varepsilon}$,

The last expression is obtained by integration in parts. The density ρ being zero for the limits, we may neglect the fact that ε_1 and ε_2 can depend on a. We therefore obtain

$$\int_{\varepsilon_1}^{\varepsilon_2} \varrho \left(\frac{\partial \overline{A]}_{\varepsilon}}{\partial \varepsilon} + A_{\varepsilon} \frac{\partial \varphi}{\partial \varepsilon} - \frac{\partial \varphi}{\partial a} \right) e^{\varphi} \, d\varepsilon = 0.$$

Now ρ being positive and e^{φ} differing from 0, we have

$$\frac{\partial \overline{A}_{\varepsilon}}{\partial \varepsilon} + \overline{A}_{\varepsilon} \frac{\partial \varphi}{\partial \varepsilon} - \frac{\partial \varphi}{\partial a} = 0.$$

The values ε_1 and ε_2 can be taken as near to each other as we like, therefore

culate $e^{-\varphi} V$ and find for it

$$\frac{2}{s} \varepsilon_{p0}.$$

It is worth noticing that (comp. GIBBS form. (377) p. 119)

$$e^{-\varphi} V = \frac{2}{s} \overline{\varepsilon_p}\Big|_{\varepsilon},$$

where $\overline{\varepsilon_p}\Big|_{\varepsilon}$ represents the average kinetic energy in the ensemble.
We therefore have

$$\overline{\varepsilon_p}\Big|_{\varepsilon} = \varepsilon_{p0}.$$

The same relation can be obtained with the help of the given formulae. Using the definition of an average value, we have

$$\overline{\varepsilon_{p2}}\Big|_{\varepsilon} = \frac{\int \varepsilon_p \Omega_\Delta}{\int \Omega_\Delta} = e^{-\varphi} \int \varepsilon_p \Omega_0 = e^{-\varphi} \int \chi (A_1 \ldots A_\lambda \ldots A_k).$$

$$(\varepsilon - \varepsilon_q (A_1 \ldots A_r \ldots A_k))^{\frac{s}{2}} dA_1 \ldots dA_k \ldots dA_k.$$

The last integral can be transformed into

$$C (\varepsilon - \varepsilon_q (A_{1_0} \ldots A_{k_0} \ldots A_{k_0}) \Omega_0 \int e^{\frac{1}{2} \sum_1^k \left\{ \left(p_k - \frac{1}{\varepsilon^2_{p0}} \left(\frac{\partial \varepsilon_q}{\partial A_r} \right)^2 - \right.}$$

we can always take care that the sign of e^φ does not change in the interval.
Now e^φ being $\dfrac{\partial V}{\partial \varepsilon}$ we can transform the last equation to

$$\overline{A}\Big|_{\varepsilon} e^\varphi = \frac{\delta V}{\partial a} + C;$$

C depending only on a. Taking for ε the least value consistent with the energy, we have to take e^φ and $\dfrac{\partial V}{\partial a}$ equal to zero and we find the same value for C.

To prove (I) we have only to keep in mind that

$$\Delta \, log \, V = \frac{1}{V} \left(\frac{\partial V}{\partial a} \Delta a + \frac{\partial V}{\partial \varepsilon} \Delta \varepsilon \right) ;$$

remembering that $e^\varphi = \dfrac{dV}{\partial \varepsilon}$ we find

$$e^{-\varphi} V \Delta \, log \, V = \overline{A}\Big|_{\varepsilon} \Delta a + \Delta \varepsilon.$$

Further $e^{-\varphi} V = \dfrac{2}{s} \overline{\varepsilon_p}\Big|_{\varepsilon}$ is equivalent to the temperature; this note shows therefore that (I) is indeed an expression which is comparable with that of thermodynamics.

$$\left. - \frac{1}{\varepsilon_{p_0}} \frac{\partial^2 \varepsilon_q}{\partial A_{\nu}^{2}} \right) \xi_{\nu}^{2} - \frac{1}{\varepsilon_{p_0}} \left(\frac{\partial \varepsilon_q}{\partial A_{\nu}} \right) \right\} d\xi_1 \ldots d\xi_{\nu} \ldots d\xi_k = C \frac{\varepsilon_{p_0} \Omega_0}{(p_1 \cdots p_{\nu} \cdots p_k)^{1/2}},$$

which can easily be seen if one remembers that the terms which enter besides p_{ν} in the exponent are very small in comparison to the p_{ν} terms. Using the given value for e^{ϑ} we obtain

$$\overline{\varepsilon_{\mu}} = (\varepsilon - \varepsilon_q (A_{1_0} \ . \ A_{\nu_0} \ldots A_{k_0})) = \varepsilon_{p_0}$$

The mean energy in the ensemble and that of the most frequently occurring systems are equal. The same is true for the force in the maximum system A_0 and the mean force $\overline{A}|_\varepsilon$.

The force exercised with respect to a parameter in a system of the energy ε, amounts to $-\dfrac{\partial \varepsilon}{\partial a}$. We therefore have

$$\overline{A}\big|_\varepsilon = - e^{-\vartheta} \int \frac{\partial \varepsilon}{\partial a} \Omega_\Delta dA_1 \ldots dA_{\nu} \ . \ dA_k.$$

The value of $\dfrac{\partial \varepsilon}{\partial a}$ can be expressed for a system for which $A_{\nu} = A_{\nu_0} + \xi_{\nu}$ and for which ξ_{ν} is not too great by

$$\frac{\partial \varepsilon}{\partial a} = \left(\frac{\partial \varepsilon}{\partial a} \right)_0 + \sum_1^k \left(\frac{\partial^2 \varepsilon}{\partial A_{\nu} \partial a} \xi_{\nu} + \tfrac{1}{2} \frac{\partial^3 \varepsilon}{\partial A_{\nu}^{2} \partial a} \xi_{\varkappa}^{2} \right) + \sum_{\nu =|= \mu} \frac{\partial^3 \varepsilon}{\partial A_{\nu} \partial A_{\mu}} \xi_{\nu} \xi_{\mu}.$$

In the integration those systems for which ξ_{ν} are great have very small influence, we can therefore adopt the given expansion for all values of ξ_{ν}. Introducing the value of Ω_Δ we easily see that the terms with $\xi_{\nu} \xi_{\mu}$ disappear in the integration. We also find:

$$\overline{A}\big|_\varepsilon = - \left(\frac{\partial \varepsilon}{\partial a} \right)_0 - \sum_1^k \frac{2}{p_{\nu}} \frac{\partial^2 \varepsilon}{\partial A_{\varkappa}^{2} \partial a} = A_0 - \sum_1^k \frac{2}{p_{\nu}} \frac{\partial^2 \varepsilon}{\partial A_{\varkappa}^{2} \partial a}.$$

In general $p_{\varkappa}$ is large compared with $\dfrac{\partial^2 \varepsilon}{\partial A_{\nu}^{2} \partial a}$, we therefore have

$$\overline{A}\big|_\varepsilon = A_0 .$$

Comparing the values of $log \ V$ and $log \ \Omega_0$, we see that we have if s is very great

$$log \ V = log \ \Omega_0 - \tfrac{1}{2} \sum_1^k log \ p_{\varkappa} + Const.$$

The sum $\sum_1^k log \ p_{\nu}$ may be neglected with respect to $log \ \Omega_0$ if k is small in comparison with s, this being the case we have

$$log\,V = log\,\Omega_0 + Const.$$

Comparing therefore $log\,\Omega_0$ for two ensembles for which the energy differs by $\Delta\varepsilon$ we find:

$$\frac{RT}{N}\,\Delta\,log\,\Omega_0 = \Delta\varepsilon + A_0\Delta a. \quad \ldots \ldots \quad (II)$$

The quantity $\frac{R}{N}\,log\,\Omega_0$ fulfills therefore the same relation as the thermodynamic entropy in the corresponding case. The correspondence however ought no longer to be considered as to be formal, all quantities relating now to real systems, i. e. to the most frequently occurring system of an ensemble, that may be identified with the system in stationary state. The function $log\,V$ showing the properties of entropy, the same will be the case for $log\,\Omega_0$.

5. I shall define the probability $W\,(A_1 .. A_r)$ of a system $(A_1 .. A_x^i .. A_k)$ as the integral of Ω taken for a region whose magnitude is given by observation and which is characterised by the quantities ΔA_x (comp. (1)). We therefore have

$$W\,(A_1 .\, A_x\, .\,A_k) = \int_{\frac{A_1-\Delta A_1}{2}} \ldots \int_{\frac{Ak-\Delta Ak}{2}}^{\frac{Ak+\Delta Ak}{2}} \Omega\,(A_1 .. A_x .. A_k).$$

Substituting in this formula the obtained value of Ω we find

$$W\,(A_1 .. A_r .. A_k) = \Omega_0 \int_{-\frac{\Delta A_1}{2}}^{\frac{\Delta A_1}{2}} \ldots \int_{-\frac{\Delta Ak}{2}}^{\frac{\Delta Ak}{2}} e^{\frac{1}{2}\sum_1^k p_\nu\,\xi^2_\nu}\, d\xi_1 .. d\xi_\nu .\, d\xi_k .$$

The ΔA_r being relatively small quantities compared with the ξ_ν, we can put this into the form

$$W\,(A_1 .. A_r .. A_k) = \Omega_0\, e^{\frac{1}{2}\sum_1^k p_\nu\xi^2_\nu}\, \Delta A_1 .. \Delta A_r .\, \Delta A_k.$$

We shall now prove that $\frac{R}{N}\,log\,W = \eta_\Delta$ shows the properties of the entropy, i.e. that

$$\eta_\Delta = \frac{R}{N}\,log\,W = \frac{R}{N}\,log\,\Omega_0 + \frac{R}{2N}\sum_1^k p_x\xi^2_\nu + Const. \quad . \quad (III)$$

answers to the relation.

$$\eta_\Delta - \eta_0 = \frac{d\varepsilon + dA}{T} . \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

Putting η_0 in stead of $\frac{R}{N} \log \Omega_0 + Const.$ we can transform (III) to

$$\eta_\Delta = \eta_0 + \frac{R}{2N} \sum_1^k p_x \xi^2, \quad . \quad . \quad . \quad . \quad (III^a)$$

The energy being the same for the systems under discussion the relation (IV) reduces to

$$\frac{R}{N} d \log W = \frac{dA}{T}$$

or

$$\eta_\Delta = \eta_0 + \frac{dA}{T}.$$

In order to prove the correspondence of the entropy η and $\frac{R}{N} \log W$, we have to show that

$$\frac{RT}{2N} \sum p_x \xi^2,$$

represents the work done if the system is brought in a reversible way from the stationary state to that indicated by Δ.

We can make this transformation reversible in two ways:

In the first place we can imagine an external field of force, applied in such a manner that the deviating state in the old ensemble is the most frequently occurring in the new and change this field of force in such a way that the most frequently occurring state passes continually from the states A through the state $A + \xi$. In the second place we can imagine fictitious forces influencing the parameters A_r in such a way that they allow the non-stationary state to exist. These forces can be changed in such a way, that the said states follow each other as a series of states of equilibrium [1]).

I will follow the second way. In order to find the forces wanted, we can take the quantities ξ_r as parameters and determine the forces Ξ_r working on the stationary system by the relation

$$e^{-\eta} V \frac{\partial \log V}{\partial \xi_r} = \Xi_r.$$

The region V to be used here is found substituting $A_{r_0} + \xi_x$ for A_x in the value found for $V(\varepsilon_1 .... A_{r_0} .)$, $A_{r_0} + \xi_r$ being now the equilibrium value for A_r.

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1) If we have for example a gas the density of which deviates from the normal we can as well by introducing a field of force as by fictitious walls change the non-stationary state into a state of equilibrium.

In this way we find for the force working on ξ_ν,

$$\Xi_\nu = \frac{RT}{N} \left\{ \left(\frac{\partial \log V}{\partial A_\nu} \right) + \left(\frac{\partial^2 \log V}{\partial A_\nu^2} \right) \xi_\nu \right\}.$$

Introducing these forces in the expression for the work we obtain

$$dA = \frac{RT}{N} \sum_1^k \left\{ \int_0^{\xi_\nu} \left\{ \left(\frac{\partial \log V}{\partial A_\nu} \right)_0 + \left(\frac{\partial^2 \log V}{\partial A_\nu^2} \right)_0 \xi_\nu \right\} d\xi_\nu \right\}$$

$$= \frac{RT}{2N} \sum_1^k \xi_\nu^2 \left(\frac{\partial^2 \log V}{\partial A_\nu^2} \right)_0,$$

the first term being zero as follows from the condition of equilibrium.

It has been shown also that $\frac{R}{N} \log W$ corresponds with entropy for a non-stationary state. For two deviating states from different ensembles the same is true, because it is always possible to pass from one to the other, passing through the stationary states of the ensembles, for which states the formula (II) is true.

6. I will shortly indicate what is obtained if we apply the above formulas to a gas (or liquid), the molecules of which answer to the hypothesis of VAN DER WAALS. Suppose that we have n perfectly rigid and elastic spherical (diameter σ) molecules in a volume V.

Let us divide the volume in k equal elements V_ν, which contain n_ν molecules. The volume of the extension in configuration can be represented, as I have shown, by

$$\frac{n!}{n_1! \, n_\nu! \, . n_k!} \left(\omega \left(\frac{n_x}{V_\nu} \right) V_\nu \right)^{n_x},$$

$\omega \, (n) = \omega \left(\frac{n_\nu}{V_\nu} \right)$ being a function of density. For the potential energy we shall use the expression

$$-\frac{a}{2} \sum_1^2 \frac{n_\nu^2}{V_\nu}.$$

The quantities n_ν are joined by the relation

$$\sum_1^k n_\nu = n.$$

The function χ of (1) has the form

$$n_1^{-n_1} \, n_\nu^{-n_\nu} \, n_\nu^{-n_\nu} \, (\omega \, (n_\nu) \, V_\nu)^{n_\nu}$$

the members n_ν being chosen for A_ν.

The condition for the most frequently occurring system is

$$- log \frac{n_x}{V_\gamma} + \frac{aN}{RT} \frac{n_\gamma}{V_\gamma} + log \, \omega(\mathrm{n}_\gamma) + \mathrm{n}_\gamma \frac{d \, log \, \omega(\mathrm{n}_\gamma)}{d\mathrm{n}_\gamma} = - t_1.$$

The quantities n_γ are normal coordinates, the value of p_ι is

$$p_\iota = - \frac{1}{n_{\gamma_0}} + \frac{2}{V_\gamma} \frac{d \, log \, \omega(\mathrm{n}_\gamma)}{d\mathrm{n}_\gamma} + \frac{\mathrm{n}_x}{V_\gamma} \frac{d^2 \, log \, \omega(\mathrm{n}_\gamma)}{d\mathrm{n}_\gamma^2} + \frac{aN}{RT} \frac{1}{V_\gamma} - \frac{N}{RT} \frac{1}{\varepsilon_p} a\mathrm{n}_\gamma^2.$$

The last term is again small in respect to the others, we therefore find

$$p_\gamma = - \frac{1}{n_\gamma} \frac{d}{a\mathrm{n}_\iota} \left(\mathrm{n}_\gamma - \mathrm{n}_\gamma^2 \frac{d \, log \, \omega \, (\mathrm{n}_\iota)}{d\mathrm{n}_\iota} - \frac{2\mathrm{n}_\gamma^2 N}{2RT} \right).$$

ε_p being $\frac{3n}{2} RT$.

If we take into consideration that the pressure π of a gas (comp. my dissertation p. 125) is expressed by

$$\pi = \frac{RT}{N} \left(\mathrm{n} - \mathrm{n}^2 \frac{d \, log \, \omega \, (\mathrm{n})}{d\mathrm{n}} - \frac{a\mathrm{n}^2}{RT} \right),$$

we can put p_γ in the form

$$p_\gamma = - \frac{1}{n_\iota} \frac{N}{RT} \frac{d\pi \, (\mathrm{n}_\gamma)}{d\mathrm{n}_\gamma}.$$

The expression $log \, V$ can easily be used to calculate the pressure.

7. The mean value of $(A_\gamma - A_{\gamma_0})^2$ i.e. of ξ^2_γ can easily be calculated. One finds for it

$$\overline{\xi^2_\gamma} = \frac{1}{p_\gamma},$$

or $p_\gamma \, \xi^2_\gamma = 1$. We can apply this formula to calculate the mean work necessary to bring the system from the normal into the deviating state, we obtain for it

$$\overline{dA} = k \frac{RT}{2N}.$$

For each quantity A_γ this mean work amounts to $\frac{RT}{2N}$ i. e. the mean work is equal to the energy pro degree of freedom.

The result has also been obtained by EINSTEIN. Indeed it can be shown that for our case the definition which EINSTEIN has given and the definition used are identical, if only it may be supposed that the path of the representing point of the system fills the space $\varepsilon =$ const. everywhere dense. EINSTEIN defines the probability of a state $A_1 .. A_x$ A_k as the fraction of a very long time T for which the

system is in the said state. I have shown [1]) that the probability in a time ensemble can be expressed by

$$C \frac{ds}{V},$$

ds being an element of the path of the system and V being the velocity of the representing point on its path. The quantity C is given by $\int \frac{ds}{V}$ integrated along the whole path.

The probability defined by EINSTEIN now can be expressed by

$$C \int \frac{ds}{V},$$

where the integration covers all those elements for which the values of A_r have the given magnitude. If the hypothesis of EINSTEIN may be used the value of this integral can be expressed by the part of the space $\varepsilon = C$ which is the limit of $d\varepsilon \, \Omega \, (A_1 .. A_r .. A_k) \, \Delta A$, if $d\varepsilon$ approaches zero, and the space has been filled in such a way with systems, that $\varrho d\varepsilon$ has a finite value if $d\varepsilon$ approaches zero.

For by EINSTEIN's hypothesis all the points for which A_x is between A_r and $A_r + \Delta A_x$ are on the path of the representing point, and the given expression represents the part of the space for which the A_r's have the given values. The integral $\int \frac{ds}{V}$ taken over the elements indicated above and $\Omega \, (A_r)$ are identical.

Using these conditions limiting, however, the generality, we have proved that the probability as defined by EINSTEIN is proportional to the entropy.

Groningen, Sept. 1911.

Physics. — *"Remarks on the relation of the method of* GIBBS *for the determination of the equation of state with that of the virial and the mean free path.* By Dr. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of December 30, 1911).

In determining the equation of state by means of statistical mechanics it is useful to introduce a function ω, which for a system of n molecules of diameter σ is given by an integral

$$\int dv_1 .. dz_n = \omega^n V^n. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1]) Comp these Proc. of Jan 28 1910, p. 804.