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Physics. — "*On the kinetic derivation of the second Law of Thermo-dynamics.*" By Dr. O. Postma. (Communicated by Prof. H. A. Lorentz.)

§ 1. In a previous paper[1]) I tried to set forth how an ensemble of molecular systems possessing only kinetic energy may be thought gradually to pass to a state in which all the combinations of place and also all the combinations of velocity of the molecules occur with the same frequency. In this final condition the molecules of by far the majority of the systems of the ensemble will, as was shown, be distributed about uniformly over the vessel and have Maxwell's distribution of velocities.

This result, however, requires some amplification.

As the problem of the distribution of place and that of the distribution of velocity were treated quite separately, the above-mentioned result implies only, that in the end the molecules will be distributed uniformly over the vessel *for all the velocities together*, and that they will have Maxwell's distribution of velocities *for the vessel considered as a whole*. This, however, is not what is generally understood by uniform distribution over the vessel and Maxwell's distribution of velocities; we mean by this that even for a limited amount of velocities the molecules will be spread about uniformly over the vessel, and that even for a limited portion of the vessel Maxwell's distribution of velocities will hold on the main. So the question remains, how this result may be obtained.

Let us first observe that in a canonical or microcanonical ensemble the uniform distribution of place and Maxwell's distribution of velocities in the latter sense is really obtained. This is very easily seen for the canonical ensemble. It is, however, also the case for a microcanonical ensemble, where the frequency of a certain distribution of place and velocity is proportional to the number of combinations possible. This number of combinations may be given in the form $Ce^{-\int\int f \log f \, d\omega d\omega}$ just as it is given in the form $Ce^{-\int f \log f \, d\omega}$ when only the distribution of the velocities is considered. So in the most frequently occurring system $-\int\int f \log f \, d\omega d\omega$ or $-H$ is maximum. With given kinetic energy this is the case, if

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1) These Proc. X, p. 390.

$f = ae^{-b(\xi^2 + \eta^2 + \zeta^2)}$, where a and b are real constants, so that for this system MAXWELL's distribution of velocities holds for any small part of the vessel, and also the density is constant throughout the vessel for one definite velocity. That for the great majority of the systems the distribution of place and velocity differs little from the maximum occurring one may be shown in the same way as it is shown when the distribution of place and velocity is considered separately.

It is, however, easy to see that if an ensemble arises, not a microcanonical one, indeed, but one, for which the mean density becomes constant for finite but small extension elements, by approximation the same result will be obtained as we have for a microcanonical ensemble, viz. uniform distribution throughout the vessel and MAXWELL's distribution of velocities, and that with greater accuracy as the elements are smaller. So we shall have a kinetic derivation of the 2nd law of thermodynamics, if we can show that an arbitrary ensemble of systems with a definite kinetic energy passes into such a "rough" microcanonical ensemble. So this has again led us to the quantity called "entropie grossière" by POINCARÉ, for if Π, the mean density over the elements d, becomes constant, $\Sigma \, \Pi \log \Pi \; d$ or the entropie grossière decreases. It seems to me that we might demonstrate in the following way that Π becomes constant in course of time.

Let us in the first place once more consider the ensemble of planets or one-dimensional moving molecules discussed in § 2 and § 3 of the above-mentioned paper. It was shown that this ensemble moves in such a way that finally all places occur equally frequently. This was the case for all the velocities together and happened just because all kinds of velocities occurred for the systems. If, however, the total amount, over which the velocities of the systems (planets or molecules) extend, is divided into small, but finite portions, it will also hold for these amounts separately, if we only take the time long enough. So when these amounts extend from ω_1 to $\omega_1 + \Delta \omega_1$, from $\omega_1 + \Delta \omega$ to $\omega_1 + 2\Delta \omega$ etc. the systems with velocities lying between ω_1 and $\omega_1 + \Delta \omega$ will finally be uniformly distributed over all the values l lying between 0 and 2π; in the same way the systems with velocities between $\omega_1 + \Delta \omega$ and $\omega_1 + 2\Delta \omega$ etc. Each of the horizontal strips of fig. 1 lying above each other contains then the same number of representing points.

If instead of an ensemble of single planets or single molecules we take an ensemble of systems of n molecules each but disregard the collisions, the same reasoning will hold. The whole of the representing points now moves, however, in a $6n$-dimensional space, and instead of the axis of distances and the axis of velocities we get now the space

of coordinates and the space of velocities. Also if we do not neglect the collisions a motion of the ensemble will take place in the moments
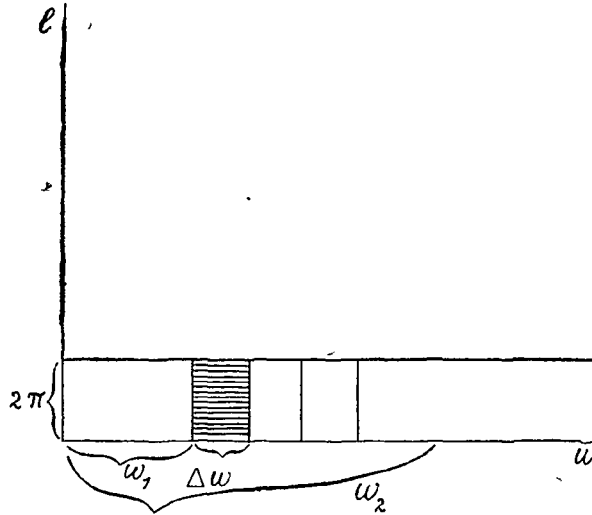

Fig. 1.

between the collisions in the indicated direction, so to the state with uniform mean density in the narrow strips extending lengthwise over a small but finite distance, bounded by the same combinations of velocities (symbolically represented by the horizontal regions a of fig. 2). In consequence of the collisions, however, the mean density in narrow vertical regions approaches uniformity. Nor need these
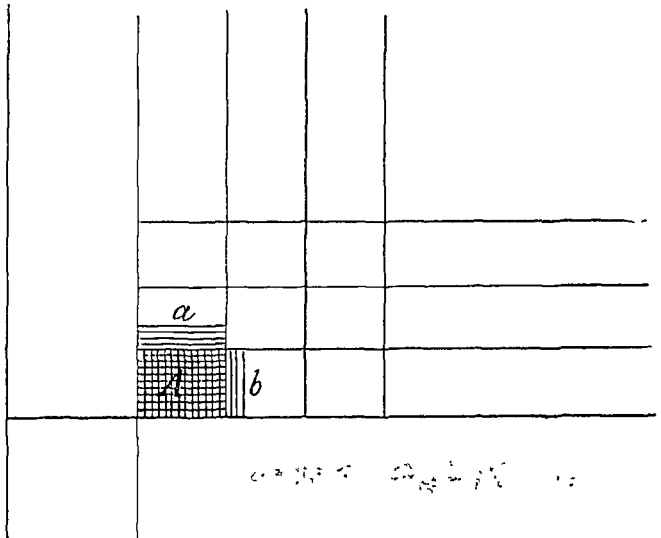
comb. of place

Fig. 2.   comb. of velocities

regions extend over the total amount of possible combinations of place, but the approach to uniformity is also found over finite small portions of this amount, (the regions b). What happens now if the two actions take place simultaneously? In the collision the representing points shift in horizontal direction, which modifies the distribution in the regions a, and the first action, which would make the distribution over the regions a uniform, is counteracted. This continues to be the case, as we think the regions a infinitely narrow; if however, we consider an element from the figure, the horizontal dimension of which is indicated by a, and the vertical dimension by b (the rectangle A), then the distribution in the elements A lying one above the other will also approach to uniformity by the first action whereas the disturbing influence-with which the second action counteracts the first, will continually decrease and approach to zero. So it seems to me that we may assume that the mean density in the elements A lying above each other becomes the same in course of time: this reasoning will, however, also hold for the elements lying side by side in horizontal direction (if we take now the second action as the principal one, and the first as the disturbing action), so that we get a "rough" microcanonical ensemble in the end [1]).

If the above reasoning is correct, we have obtained the result that every arbitrary ensemble of molecule systems with purely kinetic energy proceeds towards a state where uniform distribution of place and MAXWELL's *distribution* of velocities is most frequent. In the meantime we must assume that every system in itself has a reversible motion and so after some time it will get again very near to its initial state, and will do so repeatedly. Whether BOLTZMANN's

$$ H = \iint f \log f \, do \, d\omega $$

will decrease for the majority of the cases depends on the initial state of the ensemble. It is conceivable that this state is such that the majority of the systems are nearer to the state ·occurring finally maximum than is the case for a micro-canonical ensemble; then the H would increase instead of decrease for those systems. It is,-however, evident, that this will not be the case for an ensemble that represents a system in which recently some disturbance of equilibrium has ·taken place. For such a system H will most probably decrease.

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[1]) It would be doing GIBBS an injustice if we did not admit, that in his Statistical Mechanics he already pointed to this remaining constant of the entropie fine, in opposition to the decrease of the entropie grossière when he says treating the analogy of the coloured liquid: "If treating the elements of volume as constant ... etc." p. 145.

§ 2. Now the question may be raised what place we have to assign to Boltzmann's proof that $H = \int\int f \log f \, do \, d\omega$ would decrease for an "ungeordnetes" system with regard to the above reasoning and the one preceding it. H seems to have to decrease for such a system, which as Zermelo and others pointed out can hardly be always the case for one definite system, and can only be assumed as occurring in general for an ensemble.

In the first place we must observe with regard to this that by no means certainty prevails that a system which is in an "ungeordnet" state at a certain moment, will continue to be in such a state.

In the second place the properties of such a system, as Boltzmann applies them in the derivation of the variation of the function H in consequence of the collisions (see form. 17 and 105), can occur for one definite system with a sufficient degree of accuracy only when the elements $d\omega$, $d\lambda$ etc. occurring in these formulae, are taken rather large. There are, however, also objections to this (as that it is assumed that in a collision of two molecules the velocity-points always get outside the elements $d\omega$ and $d\omega_1$).

Independent of the size of the elements the property of being "ungeordnet" cannot occur for one definite system, it can, however, for the average of a whole ensemble (or in course of time if we think the systems taken at random from a certain ensemble).

This ensemble is formed by the whole of the possible systems obtained if we think the places and velocities of the n molecules assigned to them by chance, so that every time the chance to a certain combination of place and velocity is represented by a constant function f of the coordinates and velocities. If n is large, the majority of these systems have a distribution of place and velocity the course of which is mainly indicated by the function f. It does not hold exactly for any definite system that in the neighbourhood of every molecule the number of molecules of a certain kind are determined by the size of the spacial element considered and the f holding there, but on an average it does hold for the whole ensemble. So we may say that this ensemble represents Boltzmann's "ungeordnetes" system. On an average $\dfrac{dH}{dt}$ would, therefore, be negative for this ensemble.

On further comparison of Boltzmann's way of treatment and the results of § 1 we meet with an important point of difference. On the whole H will decrease for the majority of the systems for an arbitrary ensemble on account of the tendency towards uniformity

of density over the elements of extension indicated by A in fig. 2. This tendency proceeded from two actions, the former giving uniform density over the horizontal, the latter over the vertical regions. So we might say that the decrease of H is brought about both by the motion of the molecules (the first action) and by the collisions (the second action). The coordinates and the velocities occur also in H in the same way.

Yet BOLTZMANN states expressly that the H can only decrease in consequence of the collisions[1]) and he shows this as follows:

The change of H within a given surface is determined by

$$\frac{d}{dt}\sum_{\omega,0} log f = \iint do\, d\omega \left[\frac{\partial f}{\partial t} - log f\left(\xi\frac{\partial f}{\partial x} + \eta\frac{\partial f}{\partial y} + \zeta\frac{\partial f}{\partial z} + X\frac{\partial f}{\partial \xi} + Y\frac{\partial f}{\partial \eta} + Z\frac{\partial f}{\partial \zeta}\right)\right]$$
$$+ C_4\, (log\, f) + C_5\, (log\, f).$$

If the surface is made to join the walls of the vessel, the first term is zero, the terms with X, Y, and Z are lost if we assume that there are no external forces; C_4 and C_5 denote the change caused by the collisions. The change in consequence of the motion of the molecules is equal to:

$$-\iint do\, d\omega\, log.f\left(\xi\frac{\partial f}{\partial x} + \eta\frac{\partial f}{\partial y} + \zeta\frac{\partial f}{\partial z}\right).$$

BOLTZMANN shows that this integral is equal to:

$$\iint d\omega\, dS\, fN - \iint d\omega\, dS\, Nf\, log\, f$$

which is to be integrated over the surface S, which includes the considered gas mass. From this follows that the increase in H in consequence of the motion is equal to the quantity that is brought into the surface S by the molecules. So if the gas is left to itself, this quantity will be zero, so that H does not change in consequence of the motion, but only in consequence of the collisions[2]). No doubt we shall have to look for the explanation of this difference in result to the fact that BOLTZMANN considers the "entropie fine", whereas above the "entropie grossière" was considered. If the elements do and $d\omega$ are taken of finite size, as must be done here, the calculations which reduce the change in H to a surface integral, must not be adopted in unmodified form.

§ 3. For a kinetic derivation of the 2nd law of thermodynamics it is necessary kinetically to define a quantity which agrees in

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[1]) See: Vol. I, p. 126, note.
[2]) Cf. LORENTZ, "Abhandlungen über Theoretische Physik", Abhandl. VIII.

properties with the thermodynamic entropy. These properties are:

1. For reversible changes from one state of equilibrium into the other is $\dfrac{dQ}{T}$ the differential of a quantity which is defined as entropy;

2. in an isolated system which, as a whole, is not in equilibrium, but may be divided into parts which are, the total entropy increases. We saw above that in general the quantity introduced by BOLTZMANN

$$H = \iint f \log f \, do \, d\omega$$

decreases, also when the system does not consist of parts, each in itself in equilibrium. So if we consider a quantity proportional to $-H$ as entropy, it will certainly satisfy the second condition in by far the majority of cases. As to the first condition, this is satisfied as LORENTZ has shown[2]), if $-\dfrac{2}{3}\mu$ is taken for the constant by which

H is multiplied, in which $\mu = \dfrac{\text{mean kin. energy per mol.}}{\text{abs. temperature}}$. For a gas in stationary state

$$f = Ce^{-\frac{3m}{4k}\left(\xi^2 + \eta^2 + \zeta^2\right)} = n\sqrt{\left(\frac{3m}{4\pi k}\right)^3}\, e^{-\frac{3m}{4h}\left(\xi^2 + \eta^2 + \zeta^2\right)}$$

so that

$$-\frac{2}{3}\mu H = -\frac{2}{3}\mu N\left(\log C - \frac{3}{2}\right) =$$

$$= \frac{2}{3}\mu N \log v + \mu N \log \vartheta - \frac{2}{3}\mu N \log N - \mu N \log \frac{3m}{4\pi\mu} + \mu N$$

for which LORENTZ writes:

$$\frac{2}{3}\mu N \log v + \mu N \log \vartheta + C'.$$

At a given temperature we may, accordingly, write $N\left(\log\dfrac{N}{v} + C\right)$ also for H, in which C still contains ϑ, no longer N and v.

Besides this entropy of Boltzmann different quantities have been kinetically defined by GIBBS, which, according to him, possess the properties of the entropy. The most prominent of them is the $-\eta$ or

$-\int P \log P \, dr$, being the negative mean $\log$ of the density over the canonical ensemble which represents the system in equilibrium. As

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[2]) Cf. l.c. Abhandlung VIII.

was shown by Lorentz [1]) this quantity has the property that in reversible changes of the system the differential is equal to $\dfrac{dQ}{T}$, in which T, the modulus of the ensemble, has the properties of the temperature. This entropy was only defined by Gibbs for the state of equilibrium. When, however, we represent a gas which is not in equilibrium by a non-canonical ensemble, and define the entropy in the same way, also the second property will hold for this entropy; the quantity $\int P \log P \, d\tau$ will namely gradually decrease if the elements $d\tau$ are not taken *infinitely* small, because each portion of the ensemble with given energy approaches to a rough micro-canonical one. In the special case considered in thermodynamics that the parts of the system are in equilibrium this will also be the case [2]).

Calculating this $-\bar{\eta}$ for a perfect gas, we find, as

$$-\bar{\eta} = \frac{\bar{\varepsilon}-\psi}{T}$$

whereas

$$\bar{\varepsilon} = \frac{3}{2} NT \text{ and } -\frac{\psi}{T} = \frac{3}{2} N \log (2\pi m T) + N \log v,$$

$$-\bar{\eta} = \frac{3}{2} N + \frac{3}{2} N \log (2\pi m T) + N \log v.$$

When comparing this value with Boltzmann's entropy we must bear in mind that this T does not agree perfectly with the ϑ of Boltzmann; viz.:

$$\vartheta = \frac{mean \ kin. \ energy \ per \ mol.}{\mu} \text{ and } T = \frac{mean \ kin. \ energy \ per \ system}{\frac{3}{2} N}.$$

From this follows $T = \dfrac{2}{3} \mu \times$ mean ϑ (taken over the ensemble).

So for comparison we must take:

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[1]) See Abhandlung XI.

[2]) The objection advanced by Lorentz to this way of defining the entropy, that it would namely be difficult to understand how a non-canonical ensemble should be determined by a system that is not in equilibrium, does not seem to be conclusive to me. It is true, that the entropy and the ensemble are not determined in the same way as for a stationary system, but as we know more about the place and the velocities of the molecules or the way in which they have assumed their places and velocities, the ensemble is determined more accurately. If we e.g. know that everywhere a certain pressure and temperature prevails, we consider the ensemble as a sum of canonical ensembles, etc.

$$- \frac{2}{3}\,\mu\,\bar{\eta} = \mu N + \mu N\,log\left(\frac{4}{3}\,\pi\mu m\vartheta\right) + \frac{2}{3}\,\mu N\,log\,v,$$

for which we may also write:

$$\frac{2}{3}\,\mu N\,log\,v + \mu N\,log\,\vartheta + C\,'';$$

this $C\,''$, however, does not agree with Lorentz' $C\,'$.

In this connection 1 will finally call attention to an objection to the use of this latter entropy introduced by Gibbs.

Purely thermodynamically the entropy is determined by the diff. equation $\frac{dQ}{T} = d\eta$. So this η contains an arbitrary additive constant. This is not the case for the kinetically defined one. Boltzmann's H is entirely determined by the equation $H = \int\int f\,log\,f\,d\omega d\omega$ and so also the entropy $-\frac{2}{3}\,\mu H$. In the same way in Gibbs $-\bar{\eta} = -\int P\,log\,P\,d\tau$, if the energy is purely kinetic, which we shall assume.

The same applies to the free energy ψ, thermodynamically it contains an arbitrary additive constant, kinetically it does not. This uncertainty, however, allows us to choose the constant in thermodynamics in a convenient way, which is no more possible in the kinetic theories. This constant is now chosen in such a way that the ψ for a certain gas mass (and then also the η) is equal to the sum of the ψ's of the parts (molarly not molecularly separated). This appears clearly in Lorentz [1]). Here a gramme molecule of a certain gas is considered, and

$$\psi = -RT\,log\,v + C \text{ derived from } \frac{\partial\psi}{\partial v} = -p = -\frac{RT}{v}.$$

Now C is chosen in such a way, that $\psi = 0$ if $v = 1$, so $C = 0$ or $\psi = -RT\,log\,v$. Somewhat further it says: "Haben wir es nicht mit einer, sondern mit m Einheiten zu tun, die zusammen das Volum v füllen, so haben wir nebeneinander m-mal die Einheit in dem Volum $\frac{m}{v}$. Wir müssen also in $\psi = -RT\,log\,v$ v durch $\frac{m}{v}$ ersetzen und dann mit m multiplizieren." So by definition the ψ of the whole has here evidently been put equal to the sum of the ψ's of the parts occurring side by side in the volume v.

We may also say that this has taken place by assigning another value to C for every quantity. If namely in a volume $2v$ we had

[1]) l. c. p. 236.

two unities side by side, we should have for the first $\psi_1 = - RT \log v$, for the second $\psi_2 = - RT \log v$, so $\psi_1 + \psi_2 = - 2RT \log v$. For the total quantity we should have $\psi = - 2RT \log 2v + C$; if now we had again put $C = 0$ (so that $\psi = 0$ if $2v = 1$) then ψ would not have been $= \psi_1 + \psi_2$. The C, however, has now been chosen in such a way that $\psi = 0$ if $2v = 2$ or $C = 2RT \log 2$ and hence $\psi = - 2RT \log v = \psi_1 + \psi_2$.

In connection with this we have the property that if two quantities of different gases, being in equal volumes at the same T, are mixed in the same volume at the same T, the free energy remains the same, whereas it decreases if this is done with two quantities of the same gas. A similar property exists for the entropy (GIBBS's paradox). How is this now for the kinetically defined entropy or free energy? To answer this question we shall. successively discuss: 1 is the entropy of an homogeneous gas mass in a volume $2v$ double that of half the quantity in a volume v, 2 is the entropy of an homogeneous gas mass in a volume v greater than the sum of the entropies of two such masses forming together the first quantity each in an equal volume v; 3 is the entropy of a mixture of 2 gases equal to the sum of the entropies of the two gases separately? In the entropy of BOLTZMANN the answer is every time affirmative.

If we consider $H = N \left(\log \dfrac{N}{v} + C \right)$, then in the 1st case

$$H_1 = N_1 \left(\log \frac{N_1}{v} + C \right), \text{ so } 2H_1 = 2N_1 \left(\log \frac{N_1}{v} + C \right); \text{ further for}$$

the whole mass in the volume $2v$:

$$H = 2N_1 \left(\log \frac{2N_1}{2v} + C \right) = 2N_1 \left(\log \frac{N_1}{v} + C \right) = 2H_1.$$

In the second case:

$$H_1 = N_1 \left(\log \frac{N_1}{v} + C \right), \ H_2 = N_2 \left(\log \frac{N_1}{v} + C \right),$$

so $H_1 + H_2 = N_1 \log N_1 + N_2 \log N_2 - (N_1 + N_2)(\log v + C)$, while $H = (N_1 + N_2) \log (N_1 + N_2) - (N_1 + N_2)(\log v + C)$, so that $H < H_1 + H_2$ or the entropy of the whole is greater than the sum of the entropies of the parts.

In the 3rd case the formula for H used here does not hold, but now BOLTZMANN puts here $H = H_1 + H_2$ by definition. For a mixture of two gases BOLTZMANN puts viz.:

$$H = \iint f \log f \, d\omega \, d\omega + \iint f_1 \log f_1 \, d\omega \, d\omega.$$

However, also the questions 1 and 2 might have been answered

directly from this definition. $H = \int\int f \, log \, f \, do \, d\omega$ indicates, namely, that H of the whole $= \Sigma H$ of the parts; further we can always think the molecules divided into two parts with densities f_1 and f_2, so that $f = f_1 + f_2$,

$$(f_1 + f_2) \, log \, (f_1 + f_2) < f_1 \, log \, f_1 + f_2 \, log \, f_2 ,$$

so that also $H < H_1 + H_2$. From this latter way of treatment appears at the same time that the three properties are also valid for the entropy of BOLTZMANN if the gas is *not* in the state of equilibrium.

To answer the same questions with regard to the entropy of GIBBS we consider the formula:

$$- \bar{\eta} = \frac{3}{2} N + \frac{3}{2} N \, log \, (2\pi \, mT) + N \, log \, v.$$

As to the first question for N_1 molecules in the volume v:

$$- \bar{\eta}_1 = \frac{3}{2} N_1 + \frac{3}{2} N_1 \, log \, (2\pi \, mT) + N_1 \, log \, v ,$$

so

$$- 2\bar{\eta}_1 = 3N_1 + 3N_1 \, log \, (2\pi \, mT) + 2N_1 \, log \, v$$

and for $2N_1$ mol. in volume $2v$:

$$- \bar{\eta} = 3N_1 + 3N_1 \, log \, (2\pi \, mT) + 2N_1 \, log \, 2v ,$$

so that the entropy of the whole is *not* equal to the sum of the entropies of the parts. The *increase* in entropy (or free energy) of the whole, however, *is* always equal to the increase in entropy (or free energy) of the parts [1]).

As far as the second and third questions are concerned, we may directly take the general case of a mixture of two different gases and find then :

$$e^{-\frac{\psi}{T}} = (2\pi T)^{\frac{3N}{2}} m_1^{3\frac{N_1}{2}} m_2^{3\frac{N_2}{2}} \frac{N}{v}$$

from which :

$$- \frac{\psi}{T} = \frac{3N}{2} \, log \, (2\pi T) + \frac{3N_1}{2} \, log \, m_1 + \frac{3N_2}{2} \, log \, m_2 + N \, log \, v$$

[1]) Accordingly the equation derived by Dr. L. S. ORNSTEIN in his Thesis for the Doctorate: "Application of GIBBS's Statistical Mechanics to molecular-theoretical problems", (Leiden 1908) p. 54:

$\sum_1^k (\psi_\prime - \psi_{0\prime}) = \psi - \psi_0$ states only that the *increase* in ψ of the joint elements forms the total increase in ψ of the whole. For the "zero-state", for which $\psi_{0\prime}$ and ψ_0 hold, viz. the state in which the potential energy $= 0$, $\sum \psi_{0\prime} = \psi_0$ is by no means valid. It is exactly this "zero-state", that has been considered above.

and

$$- \bar{\eta} = \frac{3N}{2} + \frac{3N}{2} \log(2\pi T) + \frac{3N_1}{2} \log m_1 + \frac{3N_2}{3} \log m_2 + N \log v.$$

For the first substance alone we find:

$$- \bar{\eta}_1 = \frac{3N_1}{2} + \frac{3N_1}{2} \log(2\pi T) + \frac{3N_1}{2} \log m_1 + N_1 \log r,$$

for the second alone:

$$- \bar{\eta}_2 = \frac{3N_2}{2} + \frac{3N_2}{2} \log(2\pi T) + \frac{3N_2}{2} \log m_2 + N_2 \log v.$$

From this appears $- \bar{\eta} = - \bar{\eta}_1 + - \bar{\eta}_2$ or the entropy of the mixture is equal to the sum of the entropies of the gases forming the mixture, which now holds too if the component parts consist of the same gas. So there is no perfect harmony with thermodynamics: for this entropy Gibbs's paradox no longer holds.

That the $- \bar{\eta}$ of the whole volume is not equal to the $\Sigma - \bar{\eta}$ of the parts is a consequence of the fact that the extension in phase $v_1{}^{N_1} \times v_2{}^{N_2}$ is not equal to the extension $(v_1 + v_2)^{N_1 + N_2}$. In the total volume there are more possibilities of combination of place than when the volume has been divided into two separate parts. We may also say that Boltzmann's entropy just as in thermodynamics, may be divided with regard to the volume, Gibbs's entropy with regard to the molecules. If we compare the formulae :

$$II = N \left(\log \frac{N}{v} + C \right) \text{ and } \bar{\eta} = N \left(- \log v + C \right),$$

it appears that Gibbs's entropy can be brought into harmony with thermodynamics by augmenting $\bar{\eta}$ by $N \log N$ or $N (\log N + C)$. This may be done by multiplying the density e^{η} by $N^N . e^{-N}$ or $N!$ by approximation. So we should have to take for $\bar{\eta}$ the mean $\log$ of the density, not with respect to the *specific*, but with respect to the *generic* phases. [1])

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[1] When I had written the above, I observed that the last remarks are not new In the last sentence of his book Gibbs himself has already made the observation that we shall have to take $- \bar{\eta}_{gen}$ and not $- \bar{\eta}_{spec}$ as equivalent for the entropy, "except in the thermodynamics of bodies in which the number of molecules of the various kinds is constant." So it will always have to be done where the entropy of the whole is compared with that of the parts.

Nevertheless considering that Gibbs devotes so few words to the matter, I feel justified in not suppressing my remarks.