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Physics. — “*Entropy and Probability.*” By O. POSTMA. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of November 27, 1915).

§ 1. In the kinetic definition of the entropy it is necessary to determine a function S which 1. satisfies the equation $dS = \frac{dQ}{T}$ on transition from a state of equilibrium to a neighbouring one, and 2. increases in an isolated system which is not in equilibrium. Many such definitions have been given, in which now special attention was paid to one, now to the other property. The S that satisfies the second demand, must then also satisfy the first in the particular case that there is equilibrium. Additional constants evidently have no influence (by *constant* we understand here for 1: independent of energy and volume; for 2: independent of distribution of place and velocity).

In connection with the theory of quanta, however, these constants have come more into the foreground, specially for so far as they depend on the elementary region g of the extension in phase of the molecules and the number of molecules N . Of late attention has also been drawn to other properties which the entropy-function should satisfy, and more particularly: 3. the entropy of a quantity of substance is equal to the sum of the entropies of its parts. Further the dimension of the entropy has also become of more importance. When following PLANCK's example we calculate the entropy in the state of equilibrium for a perfect gas by the aid of the definition $S = k \log P$ ($P =$ probability), and make use of the condition that property (3) must be fulfilled, we come to the conclusion that the above mentioned elementary region g must be proportional to N .

Important objections are, however, adduced against this result by LORENTZ in his article: “Observations on the theory of the mono-atomic gases.”¹⁾

This result, hence also these objections are obviated by TETRODE by dividing the expression found for the entropy by $N!$. In the cited article LORENTZ observes, however, in reference to this that there is no physical reason to be found for this division.

The purpose of this article is chiefly to subject the existing difficulties to a closer examination.

§ 2. If we define the entropy by means of $S = k \log P$, the

¹⁾ Verslagen Kon. Ak. v. Wet. Amsterdam, Deel XXIII (1914) p. 515.

probability P should first be defined. In the calculus of probability it is customary to define the probability as: the ratio between the number of cases of equal chance favourable to the event and the total number of cases of equal chance. If there is not a finite number of such cases to be indicated, we get instead the ratio between the region of the favourable cases and the total region (either with a variable weight or without one).

When we wish to determine the probability of a certain state for a gas mass (and henceforth we shall only consider perfect gases) we must understand by this region the region of the possible phases of the gas-mass on definite suppositions of energy and volume. The region of the favourable cases is then the phase-extension for which the state exists, the probability of which is to be determined.

When following the example of BOLTZMANN and GIBBS we consider the weight-function at a definite energy as a constant (or constant between E and $E + dE$) we get for the probability simply the relation between two regions in the Γ -space, of $6N - 1$ or $6N$ dimensions, according as we suppose definite E_0 or variable E between E_0 and $E_0 + dE$.¹⁾

The former is the more natural supposition when with EINSTEIN we think of a time-ensemble, so that the probability is equal to the ratio between the time in which the system is in the definite state and the total time. The second is more appropriate when with GIBBS we think of possibilities existing simultaneously, so that we can imagine reality to be formed by a random choice from an ensemble. The result is of course the same in these two cases.

If we choose the former method and think the state determined by the series of the values n_1, n_2, \dots which represent the numbers of molecules, the p 's and q 's of which lie between definite limits, the molecule-phase-points, therefore, in definite elements g of the μ -space (phase-extension of the single molecule), then for definite E_0 the probability of this state is equal to the fraction:
 part of the surface $E(pq) = E_0$ in the Z -star of the Γ -space determined by that state

total area of the surface.

If we follow the second method, the denominator becomes the contents of a thin shell and the numerator that part of the shell lying inside the Z -star in question. For a perfect gas surface and shell are spherical.

Now the question suggests itself²⁾: is this fraction also equal of the

¹⁾ Here and in what follows ideas and names are made use of given in the Encyclopaed. article by P. and T. EHRENFEST.

²⁾ Cf. EHRENFEST. l. c. § 12 and § 13.

ratio of the contents of that Z -star to the contents of the "Schaale" $E(Z) = E_0$, the total of the stars, for which the energy $= E_0$, if the energy for an element g is taken $=$ that of the centre? It is easy to see that this is not the case. The fraction defined above has a variable value beginning with 0, if the surface of the shell touches the extreme points of the cells of which the star consists, increasing when the energy approaches that of the centre, and afterwards decreasing again to 0. The last mentioned fraction has a definite value when the energy is that of the star and else is zero. That the quantities are not of the same order either, appears from this that in the former case a definite distribution of state belongs to all kinds of shells, in the latter entirely to one "Schaale", whereas reversely a definite "surface" contains much fewer mutually differing distributions than a definite shell. The value of the quotient $\frac{\text{star}}{\text{"Schaale"}}$ is further too dependent on comparatively accidental circumstances to serve as measure for the probability.

The probability defined by us is, however, not easy to calculate, when as was supposed up to now, we think the elements g^N of the Γ -space arisen from cube-shaped regions g' and g'' in the configuration-extension and the extension of momentum of the single molecule. It becomes easier when we think the Γ -space divided by $E(pq)$ -surfaces and surfaces normal to them.

If we think the Γ -space divided into a Γ' -space of the distribution of place and a Γ'' -space of the distribution of momentum, we get as element: $g'^N \times$ element in Γ'' -space. Hence the chance to a certain state now becomes:

$$\frac{N!}{n_1! n_2! \dots} \times g'^N \times \text{element in } \Gamma''\text{-space}$$

total extension

in which element and extension are both thought bounded by the surfaces $E(pq) = E_0$ and $E(pq) = E_0 + dE$.

This fraction is equal to: $\frac{N!}{n_1! n_2! \dots} \times \frac{g'^N}{v^N} \times$ ratio of the spacial angles in Γ'' -space $= \frac{N!}{n_1! n_2! \dots} \times \left(\frac{g}{v}\right)^N \times \left(\frac{d\omega}{4\pi}\right)^N$, if $d\omega =$ spacial angular element for every molecule separately.

However this probability is not applicable for the entropy in the state of equilibrium. When, namely, we make the probability maximum, the obtained value P appears on calculation to depend no longer on E and v , so that $k \log P$ cannot represent the entropy

which we know from thermodynamics as a function of E and v .

Accordingly nobody has as yet made use of the real fraction of probability for the entropy; always either the numerator or the denominator was taken¹⁾ or a quantity which differed little from it. With regard to the latter it is noteworthy that in $k \log P$ terms without the factor N may be cancelled against terms with the factor N , so that for the calculation of P quantities, the ratio of which is of lower order than N , come to the same thing.

The denominator which represents the whole extension is available in the state of equilibrium, the numerator both in the state of equilibrium and outside it. In the state of equilibrium they represent the same function of E and v , so that the quotient is independent of it. We should further notice that if not the fraction of probability itself is taken, but e.g. the numerator it is of no consequence how the space is divided into elements, since the extension itself, determined by the state, is decisive. We may therefore just as well take the

usual $\frac{N!}{n_1! n_2! \dots}$.

§ 3. This expression is, however, open to the objection that the dimensions are not in order. In the expression $k \log P$ P must be a number without dimensions. If P has dimensions, the entropy will have logarithmic dimensions, i.e. increase or decrease by a definite

¹⁾ In explanation of this fact, which seems so strange at first sight, that both numerator and denominator may be taken as measure for the probability, Prof. LORENZ was so kind as to make the following remarks:

Let Q be a comparatively large region in the phase-extension, (either reduced by a function of weight or not), Q' the part of Q that is left when a certain restriction (α) is introduced (e.g. that the energy lies between two closely defined limits) and Q'' the part of Q' where besides e.g. the numbers of molecules are in the different elements $n_1, n_2 \dots$. The latter with restriction (α) may define a state S .

Now the probability of all the states satisfying (α) conjointly may be represented by $P = \frac{Q'}{Q}$ (1), or if the denominator is disregarded by $P = Q'$ (2).

But when remaining inside the limits of the restriction (α) we pay attention to the state S , we may write for its probability $P = \frac{Q''}{Q'}$ (3). This becomes for the

most probable state: $P_m = \frac{Q_m''}{Q'}$. On account of the "sharpness" of the maxima Q_m'' differs so little from Q' that (also in connection with the fact that $\log Q$ is required for the calculation) Q' may be replaced by Q_m'' . Now (2) becomes therefore: $P = Q_m''$ (4).

It is clear: P is determined by the denominator of (3) in (2), and by the numerator in (4),

value when the fundamental units are made a definite number of times larger or smaller¹⁾. The differential of the entropy will have other dimensions than the entropy itself etc.; in other words the entropy will not be a physical quantity in the usual sense²⁾. The same objection holds for the denominator. To avoid this the numerator or the denominator itself should not be taken, but it should be divided by an expression of equal dimensions, e.g. by g^N .

Planck takes the numerator divided by g^N ; at least it comes to this when he defines the "thermodynamic probability" as the number of possible ways in which a certain distribution of state can come about. Thus we get: $W = \frac{N!}{n_1! n_2! \dots}$ and now $S = k \log P$ is taken again.

This omission of g^N is an essential point; for the consequence of it is that PLANCK'S entropy function contains the element g ; the original value was independent of g .

Thus we find the value:

$$S = k \{ N \log N - \sum f \log f d\sigma - N \log d\sigma \} \text{ if } g = m^3 d\sigma$$

In this expression for S BOLTZMANN had left out the first and the third term as constants, through which he arrived at:

$$S = -k \sum f \log f d\sigma$$

$\sum f \log f d\sigma$ is BOLTZMANN'S H function.

In the state of equilibrium

$$S = k N \left\{ \frac{3}{2} \log (2 \pi m E) + \log v - \frac{3}{2} \log \left(\frac{3}{2} N \right) + \frac{3}{2} - \log g \right\}$$

follows from PLANCK'S formula, and

$$S = k N \left\{ \frac{3}{2} \log (2 \pi m E) + \log v - \frac{3}{2} \log \left(\frac{3}{2} N \right) + \frac{3}{2} - \log N \right\}.$$

from that of BOLTZMANN.

In BOLTZMANN'S formula the dimensions no longer come right; the property (3) from § 1, that the entropy of the whole is equal to the sum of the entropies of the parts, however, does hold, which property does not come true in PLANCK, if no definite assumption is made about g . To make up for this PLANCK assumes that g is proportional to N , quite arbitrarily in my opinion; the reasoning, namely, by which he tries to make plausible that this "elementary region of probability" would be proportional to N , does not hold for a perfect gas³⁾.

¹⁾ Unless also logarithmic dimensions are assigned to k , which neutralise the first. But this would be very unpractical.

²⁾ It should be remarked that GIBBS has not hesitated to state this abnormal behaviour of the entropy explicitly. Cf. on this § 4.

³⁾ Cf.: "Die gegenwärtige Bedeutung der Quantenhypothese für die kinetische Gastheorie" in "Vorträge über die kinetische Theorie der Materie und der Electricität, von MAX PLANCK u. a." Leipzig u. Berlin 1914.

It would have been better, it seems to me, to divide the "thermodynamic probability", which does not represent the originally meant probability at all now, also by $N!$, as TETRODE did for the denominator, by which property (3) is also satisfied.

Instead of the numerator, LORENTZ uses the denominator in his above-mentioned article. It may be represented by:

$$\Omega dE = \frac{(2\pi Em)^{\frac{3}{2}N-1} \cdot 2\pi m v^N}{\Gamma(\frac{3}{2}N)} dE.$$

Now Ω represents the function $\frac{dV}{dE}$ introduced by GIBBS, of which the \log forms one of the three functions for the entropy given by GIBBS (viz. φ). If we now still divide by g^N , and if we omit the terms which do not contain N as a factor, we get again PLANCK'S formula for $S = k \log P$.

TETRODE makes use of another function introduced by GIBBS¹). This function (V) does not represent the extension of the microcanonic ensemble, but the total extension below the E in question. We now find:

$$V = \frac{(2\pi Em)^{\frac{3}{2}N} \cdot v^N}{\Gamma(\frac{3}{2}N + 1)},$$

while TETRODE now puts:

$$S = k \log \frac{V}{g^N \cdot N!}.$$

from which follows:

$S = k \log \{ \frac{3}{2} \log (2\pi Em) + \log v - \frac{3}{2} \log (\frac{3}{2}N) - \log N + \frac{5}{2} - \log g \}$
which formula differs from that of PLANCK in the term $-\log N$, $\frac{5}{2}$ having taken the place of $\frac{3}{2}$. Property (3) is now satisfied without a special assumption having to be made about the elementary volume g .

Now the vindication of the division by g^N and $N!$ is still to be discussed. As far as the former is concerned, that the dimensions are not in order is of course no reason to divide particularly by g^N , which causes the result to depend on g , whereas it would otherwise be independent of it.

When it has once been assumed that $S = k \log$ extension (either of the state of equilibrium alone, of all states at definite E or of all states between 0 and E), the division by g^N may be justified by this that not a purely microcanonic ensemble must be considered, but a roughly microcanonic one, in which elements of certain

¹) H. TETRODE, "Die chemische Konstante der Gase und das elementare Wirkungsquantum". Ann. der Phys. 38 (1912).

extension g^N represent cases of equal chance. Not the absolute extent of the phase extension would therefore be of importance, but the number of finite cases of equal chance contained in it.

If we assume that a gas, not in equilibrium, can be represented by an arbitrary ensemble between narrow energy limits tending to a microcanonic ensemble which represents the gas in the state of equilibrium, the elements g^N have the practical signification that they represent the extent of the parts of the extension with regard to which the distribution has become homogeneous, whereas this is not the case inside it. Then the elements g^N would, therefore, have no fixed extent, but this would depend on the time during which the considered gas is left to itself; they can, namely, be taken smaller as the "stirring" has continued longer.

The division by $N!$ is necessary to ensure that the entropy of the whole is equal to the sum of the entropies of the parts (for so far as these parts are large with respect to the space element g'), or the extension of the whole equal to the product of the extensions of the parts. As a justification of this the following explanation may be given. If we have k separate quantities of gas, each of n molecules in a volume v , the total extension of this in the space of the distribution of place is $(v^n)^k = v^{kn}$. If, however, the volumes v are not separated from each other, but parts of a larger volume kv , we may not take v^n for the extension of the parts, because there need not be n definite molecules in every volume v , but all the molecules of the vessel can get there. It is, however, difficult to say, how much every extension changes through the parts not being separated, since the extensions are not independent of each other. For the extension of all the states, in which there are n molecules in the first volume v_1 , is for the greater part the same as that in which there are n molecules in v_2 , etc. We can, however, say what change must be effected in the total extension in consequence of the absence of the partitions.

We must, namely, take into account that the molecules from the different (k) volumes v can be interchanged, so that instead of the original extension $(v^n)^k = v^{kn}$ must be taken: $v^{kn} \times \frac{(kn)!}{(n!)^k}$ or in approximation:

$$v^{kn} \frac{(kn)^{kn}}{n^{kn}} = (kv)^{kn},$$

which is also the extension which we should have found by direct calculation of the whole. The equation

$$(v^n)^k \times \frac{(kn)!}{(n!)^k} = (kv)^{kn} \text{ or } (v^n)^k \times \frac{N!}{(n!)^k} = (kv)^N$$

can now be taken as basis to obtain an available function, which can take the place of

the extension considered up to now. We can, namely, write for this:-
 $\frac{(v^n)^k}{(n!)^k} = \frac{(kv)^N}{N!}$ or $\left(\frac{v^n}{n!}\right)^k = \frac{v^N}{N!}$. We take, therefore, now the function $\frac{v^n}{n!}$ instead of v^n , and have retained the property (3).

We arrive at the same result, when we do not take into account the interchanges between the molecules of the different parts v , but also disregard the individuality of the molecules of each part in itself, so that the number of generic phases instead of the number of specific phases has become decisive.¹⁾

The remark might be made that a consideration as the above is more of a mathematical than of a physical nature. It should, however, not be overlooked that no physical reason is given either why the entropy should have to be $S = k \log P$ or $k \log$ extension.

These functions have been taken for the entropy because they showed analogy with the thermodynamic entropy. It is, therefore, natural to make changes in these functions which render the analogy more perfect, when it is seen that the analogy is not perfect yet. We may also call the division by $N!$ such a change, through which we get a mathematically determined quantity, which satisfies the three or four conditions mentioned in § 1.

§ 4. We will now discuss for a moment the quantity for the entropy which GIBBS puts most in the foreground, viz. $-\bar{\eta} = -\int \eta dt$, in which $\eta = \log P$ and $P = \frac{D}{N}$, when D is the density of the system points in the element $d\tau$ of the Γ -space, and N the total number of system points. For a canonic ensemble $P = e^{\frac{\psi - E}{\vartheta}}$, in which attention is drawn to the fact that P has the dimensions of $\frac{1}{\text{phase extension}}$.

But then η has logarithmic dimensions, hence also $-\bar{\eta}$; as was observed above, this is no quantity in the strict sense of the word.²⁾

E and ϑ being of mutually equal dimension, also ψ must have logarithmic dimensions; ψ and E have therefore different dimensions, are therefore dissimilar quantities. Yet GIBBS speaks of ψ as of the *energy*, for which the coefficient of probability (P) = 1.

¹⁾ Cf. also: H. TETRODE, "Theoretical Determination of the entropy constant of gases and liquids". These Proc. XVII p. 1167.

²⁾ Cf. GIBBS, Statistical Mechanics, p. 19.

The difficulties may be removed if $e^{\frac{\psi-E}{g}}$ is considered as a value with dimensions 0, and then multiplied by a constant C to bring the dimensions into order.

The procedure is the same in other parts of Physics where exponential functions are used. Hence the relative density would now become $Ce^{\frac{\psi-E}{g}}$, or rather, because in this way we should get too many constants: $Ce^{-\frac{E}{g}}$, so that $\int Ce^{-\frac{E}{g}} = 1$. Now we should have to take for the entropy not the mean $-\log P$ or $-\log C + \frac{E}{g}$, but the mean $-\log (P \times \text{certain constant extension})$. If we now take g^N for this constant extension, so that the form within parentheses represents the relative number of systempoints over an extension element g^N , we get, after multiplication by the usual constant k , PLANCK'S above discussed formula.

If besides we multiply the form, the logarithm of which is taken, by $N!$, we arrive at TETRODE'S formula.

Botany. — “On the mutual effect of genotypic factors.” By Dr. TINE TAMMES. (Communicated by Prof. J. W. MOLL).

(Communicated in the meeting of November 27, 1915).

The varieties of *Linum usitatissimum* L., which I have used for my crossing experiments, show three types with regard to the breadth of the petals. In two of these, however, the length of the petal is the same.

The broadest and also the longest petal belongs to the so called Egyptian flax. I have previously¹⁾ reported on the variability-curve and the median value of both length and breadth. In the present investigation, however, the use of the mean value was to be preferred, because in some cases the measurements could not be very numerous. Since this paper only deals with the breadth, it will suffice to give the mean value of this dimension only. It is 13.4 millimetres.

The breadth of the petal was formerly taken and is still taken to be the greatest breadth. The colour of the flower of Egyptian flax is blue and has been repeatedly discussed before.

¹⁾ Das Verhalten fluktuierend variierender Merkmale bei der Bastardierung. Rec. d. Trav. bot. Néerl. Vol. VIII, 1911, p. 249.