Physics. — *"An indeterminateness in the interpretation of the entropy as log W"*. By Mrs. T. EHRENFEST-AFANASSJEWA. (Communicated by Prof. J. P. KUENEN).

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I. A certain quantity of a gas may be given, so large that it may be divided into a great number of portions — great enough for the purpose we are about to discuss — without the usual statistical treatment of the parts losing its value.

Regarding the matter from a thermodynamic point of view we assume:

1. that the entropy of every system strives to attain its maximum.

2. that the entropy of the total mass of gas is equal to the sum of the entropies of the parts.

If in accordance with the kinetic theory, we take the entropy to be the logarithm of the probability of the state of the system, we get the following theses as the analogues of those just given:

1. The state of every system endeavours to approach the greatest probability;

2. The logarithm of the probability of the state of the total mass of gas is equal to the sum of the logarithms of the probability of the states of its parts; or in other words: the probability of the state of the whole is equal to the product of the probability of the states of its parts.

At the same time it may easily be seen that the latter theses are only correct provided the combinations with which we reckon in the determination of the probability of the state of the whole are submitted to certain limitations, which are quite arbitrary *from the combinationary point of view.*

II. We will illustrate this by a simple example, which depends only on the calculus of combinations.

Let us suppose 27 tables, each provided with three holes. In each of the holes a red or a black ball must come to lie. The colour of the ball may be decided by a lottery, in which the chance of drawing a red ball is $^2/_3$, and of a black ball $^1/_3$.

In this case for each table separately — if we still distinguish between the three different holes [1]) — the most probable division of the balls is: two red ones and one black one. For this the probability is [2])

$$\frac{2}{3} \times \frac{2}{3} \times \frac{1}{3} \times \frac{3!}{2!} = \frac{12}{27}.$$

We must now ask: what is the most probable distribution of the combinations over all the 27 tables? We can here still distinguish between the tables. As the most probable distribution we get that in which on only twelve tables two red balls and one black ball lie, on eight of the others three red ones, on six 2 black ones and one red one, and on the last one three black balls. For this distribution the probability is expressed by

$$W_m = \left(\frac{12}{27}\right)^{12} \cdot \left(\frac{8}{27}\right)^{8} \cdot \left(\frac{6}{27}\right)^{6} \left(\frac{1}{27}\right)^{1} \cdot \frac{27!}{6!\,8!\,12!}.$$

On the other hand, the chance that on each of the 27 tables uniformly two red balls and one black ball should come to lie is given by

$$W_u = \left(\frac{12}{27}\right)^{27}.$$

The ratio between the two is

$$\frac{W_u}{W_m} = \frac{12^{27-12} \,.\, 6!\,8!\,12!}{8^8 \,.\, 6^6 \,.\, 27!},$$

which is very much smaller than 1 [3]).

Let us now suppose the number of balls that can lie on a table, and also the number of tables to be greater; the number of different typical possibilities of division on each table separately (varying from all red to all black) then rises, as also the number of ways in which we can find these types of division spread over the collective tables.

The chance of the most probable division for one particular table becomes *smaller*. The probability W_u, that just this division will be found repeated on every table, becomes therefore represented by a high power of a very small fraction.

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[1]) That is to say, if for a particular combination (e.g. 1 red, 2 black) we count as separate possibilities the cases in which differently coloured balls lie in a given hole.

[2]) The chance of all three being red is $\frac{8}{27}$, of one red and two black $\frac{6}{27}$, of all three black $\frac{1}{27}$.

[3]) For $\frac{6!}{6^6} \cdot \frac{8!}{8^8} \cdot \frac{12!\,12^{27-12}}{27!} = \frac{6!}{6^6} \cdot \frac{8!}{8^8} \cdot \frac{12}{13} \cdot \frac{12}{14} \cdots \frac{12}{27}$, in which further $\frac{6!}{6^6} < \frac{1}{64}$, $\frac{8!}{8^8} < \frac{1}{400}$, $\frac{12}{13} < 1$, $\frac{12}{14} < 1, \ldots \frac{12}{27} < 1$.

On the other hand, the chance W_m for the realisation of that case, in which the different types are found represented amongst the collective tables in proportion to their probability, will contain a large permutation-factor, and consequently — with a sufficiently large number of tables the ratio W_u/W_m may reach any degree of smallness. It makes a great difference, therefore, — and of course not only to the calculation of the maximum — whether we take the tables collectively as an object of higher order in the calculation of combinations or whether we determine the probability for each table separately and calculate that of the whole as product of the separate probabilities.

III. Suppose that the number of tables and holes for each table are not yet given, but only the total number of hollows in all the tables together, and that it was left to our choice to divide them amongst the tables, then an opinion as to what was the most probable division would be even more arbitrary.

IV. It is obvious, that the above considerations may be applied to the gas, taking into consideration, where necessary, additional conditions.

If we introduce the restriction that in the parts only we attend to all the possible permutations, in defining the most probable division, and that in the system as a whole we do not take into consideration any further permutations between these parts, *only then* does the probability for the state of the whole appear as the product of the probability of the states of the parts.

If on the other hand the total system is regarded as a new object for combinations, an object of a higher order, the probability of the distribution of a special state in the whole is not equal to the product of the probabilities of the parts corresponding to this state. The latter must be corrected by a certain permutation-factor, the magnitude of which is dependent upon the number of the parts, that is either upon the fineness of the division to be chosen at will, or — with a permanently fixed fineness of division — upon the magnitude of the total system.

The question arises: with which *log W* should the entropy be identified?

Only when the said permutation-factor is neglected can it be said that the tending of the parts towards the maximum of their entropy brings with it a striving towards a maximum of the entropy of the whole.

If we adopt the latter view, in other words if we say that the *log W* of a system is *almost the same* as the sum of *log w* of its parts, at the most a sign of inequality is changed into a sign of equality. It is not justifiable, however, *to reverse* the sign of inequality. But this is just what happens when, for instance, the uniform distribution of density in a gas is regarded as the most probable state, and in order to calculate the probability of a distribution slightly deviating from this the relation

$$\log W = \Sigma \log w,$$

is taken as the basis, for in this way each deviating distribution appears as a less probable one [1]).

V The above analysis is by no means intended to call into question the validity of calculations similar to those indicated in the preceding paragraph, as these rest on the thesis that the entropy of the whole is equal to the sum of the entropies of the parts, a thesis that probably is physically better justified than the combinatory reasonings, at least in the circumstances in which they are applied. The analysis is merely intended to make clear that the *decision of the question whether the probability of the state of a system has reached its maximum or not, depends upon the point of view of the investigator*, and that the *ideas formed from purely combinatory reasonings do not form a satisfactory or conclusive foundation to direct our choice amongst many different standpoints to any one in particular*; further that the choice of our standpoint is made on the ground of various physical intuitions, which are outside the pale of the combination-calculus as such.

That is to say, that the combinational reasonings in question cannot be deduced from a higher principle which may be said to rule nature.

VI. We can show this more particularly in the case of a gas. Let us bring together two cubic centimetres of gas at different temperatures. If it should depend upon the "probability principle" which is to happen, it would be quite indefinite whether an equalisation of temperature would take place or not. It would depend upon the question of which is more important in nature; one cubic centimetre or trillions of cubic centimetres. In the latter case our two cubic centimetres might just be those members of our trillion

1) R. Fürth. *Ueber die Entropie eines realen Gases als Funktion der mittleren räumlichen Temperatur- und Dichteverteilung.* Phys. Zschr. **18**, p. 395—400, 1917.

system, which ought to have different temperatures in order that the whole may get the most probable division of temperature over its parts (trillion tables, and upon each of them million balls). If it is advanced against this that an inequality of this kind must continually appear in precisely the same cubic centimetres, so that *our* two portions of gas may still equalize their temperature, it must not be forgotten that this demands that at the same moment another arbitrary pair of cubic centimetres would be obliged to change temperature in just the opposite direction.

Further it must be remembered that in the case when the subdivision is continued as far as the single molecules we do actually take up the latter standpoint: the momentary kinetic energy accorded to each separate molecule is in itself not the most probable; over a sufficiently large number of molecules, however, the velocities are divided in such a manner that we can only talk of the most probable distribution for the whole of these molecules (quadrillion tables with one ball on each, or, what comes to the same, one table with quadrillion balls).