

2. *The Structure of the Atom.*
By Professor Sir J. J. THOMSON, F.R.S.

3. *The Relation between Entropy and Probability.*
By Professor H. A. LORENTZ.

The important problem of the interpretation of entropy in the terms of molecular theory may be considered as having been solved by the physicists who developed the methods of modern statistical mechanics. It is now universally recognised that the entropy of a body in a certain state is intimately connected with the probability of that state, the relation between the two being expressed by Boltzmann's formula

$$S = \frac{R}{N} \log P,$$

where S is the entropy, P the probability, R the gas constant for a gramme-molecule and N the number of molecules in a gramme-molecule.

The question is, however, in what way the probability is to be evaluated.

In order to find P , and consequently S , as a definite function of the energy E and appropriate geometrical parameters, such as the volume v in the case of a gas or a liquid, one may proceed as follows. Let $q_1, q_2 \dots q_s$ be the co-ordinates which determine the position of the particles of the body, $p_1, p_2 \dots p_s$ the corresponding momenta. Conceive a polydimensional space (the 'extension in phase') in which the $2s$ quantities $q_1, \dots p_s$ are taken as co-ordinates, so that the state of the body is represented by a single point. Consider further two surfaces in the space ($q_1, \dots p_s$), the first of which is characterised by the condition that at each of its points the energy has a definite value E , whereas the second corresponds in the same way to the value $E + dE$. Then the volume of the layer between these surfaces will be proportional to dE and may therefore be represented by PdE , the factor P being a function of E and also of the volume v , the value of which is to be taken into account in the calculation. Now, if the quantity P , defined in this way, is substituted in Boltzmann's formula, S becomes identical with the thermodynamical entropy. In the case of a mono-atomic gas, this may be shown by direct calculation and the proposition may be extended to other bodies by means of a mode of reasoning (based on a certain assumption) which cannot now be considered.

The above method is closely connected with Gibbs's microcanonical ensembles, and it is to be remarked that the introduction of canonical ensembles likewise enables us to determine a thermodynamical function. As is well known, an ensemble of the latter kind consists of a very great number of systems or bodies, whose representative points are distributed throughout the extension in phase with a density given by the expression

$$Ae^{\frac{\Psi - E}{\Theta}}$$

where A is the total number of systems, Θ a constant that plays the part of the temperature, and Ψ another constant that proves to be the 'free energy.' Now, if $d\Omega$ is an element of the extension in phase, we have

$$\int e^{\frac{\Psi - E}{\Theta}} d\Omega = 1$$

(because the integral of $Ae^{\frac{\Psi - E}{\Theta}} d\Omega$ must give the total number of systems) or

$$e^{\frac{\Psi}{\Theta}} = \int e^{-\frac{E}{\Theta}} d\Omega.$$

By this equation one can calculate the free energy for a given temperature and a given value of the volume. The result will be connected with the value of the entropy deduced from Boltzmann's formula, in the way that is known from thermodynamics.

On account of the enormous number of molecules contained in a body, Boltzmann's formula has a very remarkable property, namely that great changes in the value assigned to the probability P have no appreciable influence on the entropy S .

Consider, for instance, the case of a mono-atomic gas. If the number of its molecules is n , one finds

$$P = C v^n E^{\frac{3n}{2} - 1}$$

C being a determinate constant factor. Hence, if we omit the corresponding term in the entropy,

$$S = n \frac{R}{N} \log \left(v E^{\frac{3}{2} - \frac{1}{n}} \right),$$

for which we may write, since n is a very great number,

$$S = n \frac{R}{N} \log \left(v E^{\frac{3}{2}} \right),$$

an expression which will lead to a number that is neither very small nor very great, when the mass considered is comparable with a gramme-molecule.

Now, if the value of P is multiplied by the number of molecules n , or even by a high power of this number, such as n^{100} , this does not produce any appreciable difference in the value of S . Indeed, S is increased in these cases by $\frac{R}{N} \log n$, or $100 \frac{R}{N} \log n$, and this is very small in comparison with the above value, because for large numbers the logarithm is very much smaller than the number itself. Boltzmann's formula is therefore wholly insensible to such factors as n or n^{100} in the value of the probability.

The way in which, in the case of a gas, P depends on the volume v , may be understood by a very simple reasoning. If the n molecules are distributed at random over a volume v , the probability that they shall all lie in one half of it is $P' = \frac{1}{2^n}$, whereas $P=1$ if all possible distributions are taken together. The difference between the two values is enormous. Yet the corresponding difference in the entropy is no more than $n \frac{R}{N} \log 2$, an expression really corresponding to the change in the entropy when the volume is reduced to half its original value.

In virtue of the property of Boltzmann's formula here pointed out, one is free to a great extent in the choice of the value of P . The probability, for instance, that exactly $\frac{n}{2}$ molecules lie in one half of the volume v and the remaining ones in the other half—which is the most probable distribution—is given by

$$P'' = \frac{1}{2^n} \frac{n!}{\left(\frac{n}{2}!\right)^2},$$

or, with a sufficient approximation

$$P'' = \sqrt{\frac{2}{n}}.$$

This is much smaller than unity, showing that the exact realisation of the most probable distribution is very improbable. Yet it does not make any difference worth considering in the value of S , whether this small value or the value 1 is substituted in the formula. This exemplifies that, in order to determine the value of the entropy, one may as well take for P the probability of the most probable state of things, as the much higher value that is obtained if all possible states are included.

4. *The Structure of the Atom.* By Professor E. RUTHERFORD, F.R.S.

5. *The Electrical Resistance of Thin Metallic Films.*

By W. F. G. SWANN, A.R.C.S., D.Sc.

If the specific resistance of a film is plotted against its time of deposit, the curve shows, as is well known, a sharp bend. The theory usually given