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V. *On the Probabilities of Molecular Configurations.* By
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WITH reference to Sir William Thomson's recently re-
published kinetic explanation of dissipation of energy,
I should like to lay some few remarks upon the subject of the
probabilities of molecular configurations before the readers of
the Philosophical Magazine.

Let us imagine a volume V divided into n equal parts or
"elements," and suppose in that volume N points to be con-
tained. These points may represent ordinary material mole-
cules for the sake of investigating the distribution of density
in a fluid medium, phenomena of diffusion, and some further
cases of material equilibrium; in other problems, however,
the points may be taken to represent anything else. They
may mean elementary chemical atoms in discussing dissocia-
tion and other cases of chemical equilibrium; or ends of lines
drawn from a fixed point so as to represent the speeds of
various molecules at a given time (in order to investigate the
distribution of velocities in a crowd of molecules); or, again,
in molecular theory of capillary action, they may be regarded
as ends of lines constituting a (similar) space-diagram intended
to represent in direction and magnitude all the forces ex-
perienced at a given time by a molecule of a liquid.

To take the simplest case, let us find the probability of the
following arrangement of N molecules in n elements of volume
Suppose the first element contains N_1 molecules, the second
 N_2 molecules, ..., the n th contains N_n molecules. This
particular arrangement may be symbolized thus :—

$$(N_1, N_2, \dots, N_n); \dots \dots \dots (1)$$

its probability will be denoted by Q . It will be admitted at
first that the chance of any given molecule being in a given
element does not depend in any way upon the simultaneous
presence, in that element, of any number of other molecules.

Could we endow with one, and only one, molecule every
element of volume, we should be able to realize the corre-
sponding arrangement of molecules in

$$N(N-1) \dots 3.2.1 \text{ or } N! \dots \dots \dots (2)$$

distinct manners. Now in the case before us the first element
contains by supposition not one but N_1 molecules; and

* Communicated by the Author.

mutual interchange between these, being now limited to the interior of the first element, will not lead to new and distinct molecular configurations. Since to the N_1 molecules in the second element, to the N_2 molecules in the third, &c., the same remark applies, the arrangement (1) cannot be realizable but in

$$\frac{N!}{N_1!N_2!\dots N_n!} \dots \dots \dots (3)$$

distinct manners; and if we agree to put $0! = 1$ the expression just given will not be altered in the case in which some of the N_i are equal to zero. To find the value of the probability Q we have to divide (3) by the sum of all terms of the form (3) which are consistent with the condition

$$N_1 + N_2 + \dots + N_n = N. \dots \dots \dots (4)$$

Accordingly, we obtain

$$Q = \frac{N!}{n^N N_1! N_2! \dots N_n!} \dots \dots \dots (5)$$

From this it follows at once that the smallest value of Q , say Q' , is assumed in the case in which of the numbers N_1, N_2, \dots, N_n all are equal to zero, except one, which is therefore equal to N ; and that the greatest value of Q (or Q'' say) corresponds to the case

$$N_1 = N_2 = \dots = N_n = \frac{N}{n} \dots \dots \dots (6)$$

The corresponding probabilities are

$$Q' = \frac{1}{n^N} \text{ and } Q'' = \frac{N!}{n^N \left[\left(\frac{N}{n} \right)! \right]^n}; \dots \dots \dots (7)$$

hence

$$\frac{Q'}{Q''} = \frac{\left[\left(\frac{N}{n} \right)! \right]^n}{N!}, \dots \dots \dots (8)$$

or, approximately, N and N/n being very large,

$$= \frac{1}{n^{N+\frac{1}{2}n}} \sqrt{(2\pi N)^{n-1}},$$

a very small fraction for any large value of N . In words: that all the molecules should be accumulated in *one* element is the most improbable, and that they should be evenly distributed

among all elements is the most probable event*. Thus the arrangement of a given number of molecules in a given volume, the probability of which is greatest, is found to coincide with what would actually take place in the case of a homogeneous fluid not acted on by external forces.

If in a given volume molecules of different kinds are present, the ultimate arrangement is easily seen to coincide again with that the probability of which is greatest.

To interpret such results, observe that the calculation of probability wholly depends upon the assumption that the probability of a molecule being in a definite element is not affected by the fact of other molecules being there at the same time. The conclusion then we have to draw every time the actual arrangement of molecules coincides with that the probability of which is greatest, is clearly that in such cases no disturbing forces are operative, the effect of which would be to influence the chances of some elements or of certain molecules and thus to affect pure probabilities hitherto considered.

In many and various cases, however, the actual ultimate arrangement of molecules is found to differ immensely from what we should have expected on grounds of purely geometrical probability; and the same may be said with respect to chemical or elementary atoms, their arrangement being in all cases (except when total dissociation occurs) of a kind which we should have expected to be highly improbable.

It would seem therefore that these are the cases in which it is right to introduce the idea of molecular and atomic forces. Let us admit, as a general principle in molecular theory, *that atoms and molecules, unless they are subjected to mutual or external forces, tend to assume that kind of ultimate arrangement the (pure) probability of which is greatest.* This principle

* Highly instructive from this point of view is Joule's celebrated experiment of 1844, in which air compressed in a vessel (A) was allowed to rush into another equal vessel (B) which was previously exhausted. Take every one of the vessels as an "element," as defined above; the two taken together will represent what has been called "Volume V." Consider the state of things in the moment when the stopcock is suddenly opened and the first molecule is about to escape from A into B. In that initial (artificially produced) configuration the arrangement of molecules is exactly that which in this case is the most improbable (n being here = 2). In the final condition of uniform density and temperature, on the other hand, the arrangement is reached the probability of which is greatest.

Thus, in this case,

$$\frac{Q'}{Q''} = \frac{1}{2^N} \sqrt{\frac{\pi N}{2}},$$

and N being of the order of 10^{24} , the initial distribution is seen to be exceedingly important if compared with the final.

is seen then to be in exact analogy with Newton's first Law of Motion. Every time a material point does not move in a straight line with constant velocity, that point is considered to be acted on by force. Every time molecules or atoms assume some steady state, which is not that the probability of which is greatest, we will say they are compelled by force to do so.

The relativity of the idea of force in molecular theory will be perceived as clearly as it is in ordinary dynamics.

VI. Notes on the Theory of the Transformer.

By HENRY A. ROWLAND *.

AS ordinarily treated the coefficient of self and mutual induction of transformers is assumed to be a constant, and many false conclusions are thus drawn from it.

I propose to treat the theory in general, taking account of the hysteresis as well as the variation in the magnetic permeability of the iron †.

The quantity p as used by Maxwell is the number of lines of magnetic induction enclosed by the given conductor. This will be equal to the number of turns of the wire into the electric current multiplied by the magnetic permeability and a constant. But the magnetic permeability is not a constant but a function of the magnetizing force, and hence we must write

$$p = Bny + C(ny)^3 + \delta(ny)^5 + \&c.$$

Where B , C , &c. are constants, n is the number of turns, and y the strength of current.

In this series only the odd powers of y can enter in order to express the fact that reversal of the current produces a negative magnetization equal in amount to the direct magnetization produced by a direct current. This is only approximately true, however, and we shall presently correct it by the introduction of hysteresis. It is, however, very nearly true for a succession of electric waves.

To introduce hysteresis, first suppose the current to be alternating so that $y = c \sin(bt + e)$, where t is the time and e the phase. The introduction of a term $A \cos(bt + e)$ into

* From the Johns Hopkins University Circular. Communicated by the Author.

† The problem is treated by the method of magnetic circuit first applied by me to iron bars in my paper on "Magnetic Distribution" (Phil. Mag. 1875, l. pp. 257, 348) and afterwards to the magnetic circuit of dynamos at the Electrical Conference at Philadelphia in 1884. I also used the same method in my paper on "Magnetic Permeability" in 1873 (Phil. Mag. 1873, xlvi. p. 140).