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mation of ammonium-carbonate, the carbonic acid being resorbed from the air. There is no doubt that this resorption takes place; and expecting that the salt mentioned might cause the ripening, I added 10 pCt. carbonate of ammonium to the solution. However without the desired result, even after the solution was several months old.

I then took into consideration whether the carmine might perhaps resorb oxygen from the air, and would need to be oxygenated; and this proved to be case.

When putting together:

10 gr. carmine powder,

10 cc. ammonia,

20 cc. hydrogenperoxyd,

the mixture boiled for a short time in a glass receiver, then cooled down (for instance by letting the receiver float in water in a half-filled cylinderglass), a ripe carmine solution is obtained in a few minutes, which, treated in the above-mentioned way, produces fully 9 gr.¹⁾ of an almost black ammoniumcarmine, which is entirely, sometimes a little unclearly, soluble in water.

Instead of boiling with hydrogen-peroxyd an equal quantity of a 1 pCt. solution of kaliumpermanganate can be taken as well, although in this case the oxygenation is easily carried too far.

Physics. — "*The entropy of radiation*" (II). By J. D. VAN DER WAALS JR. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

IV.

Distribution of the vibrations of the molecules.

In the second part of his "Vorlesungen über Gastheorie" Prof. BOLTZMANN discusses the way in which the intramolecular energy is distributed over the different molecules. He finds that the chance

¹⁾ If *dry* carmine has been used. But carmine as it is sold, frequently contains 10 pCt. or more water, though it may seem to be dry.

that a molecule belongs to a certain group, may be represented by:

$$A_1 e^{-2hE_1} dp_1 dp_2 \dots dp_\mu dq_1 dq_2 \dots dq_\mu.$$

In this A_1 and h are constants, E_1 the energy of the intramolecular motion, $p_1 \dots p_\mu$ the coordinates, which determine that motion and $q_1 \dots q_\mu$ the momenta corresponding to those coordinates.

From this would follow, that the chance that the amplitude a_{x1} of the vibration of a molecule is contained within certain limits, is represented by:

$$\frac{1}{\beta \sqrt{\pi}} e^{-\frac{a_{x1}^2}{\beta^2}} da_{x1}.$$

However we cannot accept this result without further proof. The motion, which we are considering, and which is the cause of radiation, is necessarily damped, so that between two collisions a molecule has lost part of its intramolecular energy; moreover the molecule has absorbed energy from the field. For such a motion the proof of Prof. BOLTZMANN does no longer hold.

In order to find the distribution of the amplitudes we shall have to take into consideration two causes of change: the collisions and the electric forces.

First I shall examine the influence of the electric forces, and then inquire whether the collisions of the molecules will modify the distribution brought about by the electric forces. I shall make the same assumptions about the construction of a molecule as Prof. LORENTZ did¹⁾, i. e.:

a. I assume every molecule to contain an ion charged with electricity.

b. That ion has a position of equilibrium in the molecule, from which it can move in all directions, and to which it is driven back with a force, proportional to the deviation.

c. The mass of the ion is so small compared to that of the rest of the molecule, that when the molecule is vibrating, the ion alone may be considered to move.

d. The remaining part of the molecule is charged opposite to the charge of the ion and that in such a way that, when the ion is in its position of equilibrium, the electric forces, exercised by

¹⁾ Arch. Neerl. XXV, 5, 1892.

the ion, are entirely destroyed by the remaining part of the molecule. From these assumptions we find for the equation of motion of an ion ¹⁾:

$$m \frac{d^2 x}{dt^2} = -f(x-x_1) + 4\pi V^2 \frac{d^2 x}{dt^2} \int \rho_0 \omega d\tau + \frac{e^2}{V} \frac{d^3 x}{dt^3} + 4\pi V^2 e f + e \left(\frac{dy}{dt} N - \frac{dz}{dt} M \right).$$

Here m represents the mass of the ion, f a constant factor, x the coordinate of the ion, x_1 that of the position of equilibrium of the ion, e the electric charge.

The term $-f(x-x_1)$ is due to the fact that an ion has a position of equilibrium, towards which it is driven back. The second and third term of the right hand side indicate the influence of the electric forces exercised by the molecule itself. The second term may be transferred with the negative sign to the left hand side; it is evident that it gives then an apparent change of the mass of the ion. If we represent by m the mass of the ion, modified in such a way, we may leave this term further out of account. The third term has always the sign opposite to that of the velocity and explains the damping, which a vibrating particle experiences in consequence of the fact that part of the energy is radiated into space. The three last terms express the forces, exercised by the surrounding molecules on the ion. Prof. LORENTZ has pointed out that the fourth term is great compared to the fifth and sixth. For f we shall take the electric force, as it is in the position of equilibrium of the ion. The force $4\pi V^2 e f$, which we take then into consideration, acts on the ion and on the rest of the molecule with the same amount but in an opposite direction, and has therefore only influence on the vibration of the molecule. On the other hand, the forces which we neglect:

$$4\pi V^2 e \frac{df}{dx}(x-x_1) + e \left(\frac{dy}{dt} N - \frac{dz}{dt} M \right)$$

would also give a progressive motion to the centre of gravity of the molecule. Afterwards I hope to discuss the influence of these forces.

For the external force f we shall write:

¹⁾ LORENTZ, loc. cit. equation I § 90 in connection with equations 111 and 112.

$$f_1 \cos \frac{2\pi t}{T} + f_2 \sin \frac{2\pi t}{T}$$

and we shall take constants for f_1 and f_2 . As a molecule is actually subjected to an alternating electric force, the amplitude and the phasis of which vary with the time, we get in this way a solution which will hold with approximation for a short time only; but which will yet be sufficient to conclude from the condition at a given moment to that of a short time Δt after. The equation which we have to solve, is therefore reduced to:

$$m \frac{d^2 x}{dt^2} = -f(x-x_1) + \frac{e^2}{V} \frac{d^3 x}{dt^3} + 4\pi V^2 e \left(f_1 \cos \frac{2\pi t}{T} + f_2 \sin \frac{2\pi t}{T} \right)$$

or if we put $a_x = e(x-x_1)$:

$$m \frac{d^2 a_x}{dt^2} = -f a_x + \frac{e^2}{V} \frac{d^3 a_x}{dt^3} + 4\pi V^2 e^2 \left(f_1 \cos \frac{2\pi t}{T} + f_2 \sin \frac{2\pi t}{T} \right)$$

The solution of this is:

$$a_x = \left(a'_{x1} \cos \frac{2\pi t}{T} + a'_{x2} \sin \frac{2\pi t}{T} \right) e^{-kt} + b_{x1} \cos \frac{2\pi t}{T} + b_{x2} \sin \frac{2\pi t}{T} .$$

By substituting in the equation for $m \frac{d^2 a_x}{dt^2}$ this value of a_x and by equating the coefficients of

$$e^{-kt} \cos \frac{2\pi t}{T}, \quad e^{-kt} \sin \frac{2\pi t}{T}, \quad \cos \frac{2\pi t}{T} \quad \text{and} \quad \sin \frac{2\pi t}{T}$$

separately to zero, we find the following four equations:

$$\begin{aligned} a_{x1} m \left(\frac{4\pi^2}{T^2} - k^2 \right) - f a_{x1} + \frac{e^2}{V} a_{x1} \left(-k^3 + 3k \frac{4\pi^2}{T^2} \right) + 2 a_{x2} m k \frac{2\pi}{T} + \\ + \frac{e^2}{V} a_{x2} \left[3k^2 \frac{2\pi}{T} - \left(\frac{2\pi}{T} \right)^3 \right] = 0 \end{aligned}$$

$$\begin{aligned} a_{x2} m \left(\frac{4\pi^2}{T^2} - k^2 \right) - f a_{x2} + \frac{e^2}{V} a_{x2} \left(-k^3 + 3k \frac{4\pi^2}{T^2} \right) - 2 a_{x1} m k \frac{2\pi}{T} + \\ + \frac{e^2}{V} a_{x1} \left[-3k^2 \frac{2\pi}{T} + \left(\frac{2\pi}{T} \right)^3 \right] = 0 \end{aligned}$$

$$b_{x1} m \frac{4 \pi^2}{T^2} - f b_{x1} - b_{x2} \frac{e^2}{V} \left(\frac{2 \pi}{T} \right)^3 + 4 \pi V^2 e^2 f_1 = 0$$

$$b_{x2} m \frac{4 \pi^2}{T^2} - f b_{x2} + b_{x1} \frac{e^2}{V} \left(\frac{2 \pi}{T} \right)^3 + 4 \pi V^2 e^2 f_2 = 0 .$$

From the first and the second equations follows :

$$m \left(\frac{4 \pi^2}{T^2} - k^2 \right) - f + \frac{e^2}{V} \left(-k^3 + 3 k \frac{4 \pi^2}{T^2} \right) = 0$$

$$2 m k + \frac{e^2}{V} \left(3 k^2 - \frac{4 \pi^2}{T^2} \right) = 0 .$$

from which T and k may be calculated.

a'_{x1} and a'_{x2} are constants which may be arbitrarily chosen. The quantities b_{x1} and b_{x2} are not arbitrary, but are determined from the third and the fourth equations as follows :

$$b_{x1} = \frac{4 \pi V^2 e^2 \left[\left(m \frac{4 \pi^2}{T^2} - f \right) f_1 + \frac{e^2}{V} \left(\frac{2 \pi}{T} \right)^3 f_2 \right]}{\left(m \frac{4 \pi^2}{T^2} - f \right)^2 + \frac{e^4}{V^2} \left(\frac{2 \pi}{T} \right)^6}$$

$$b_{x2} = \frac{4 \pi V^2 e^2 \left[-\frac{e^2}{V} \left(\frac{2 \pi}{T} \right)^3 f_1 + \left(m \frac{4 \pi^2}{T^2} - f \right) f_2 \right]}{\left(m \frac{4 \pi^2}{T^2} - f \right)^2 + \frac{e^4}{V^2} \left(\frac{2 \pi}{T} \right)^6}$$

We shall represent this by :

$$b_{x1} = p f_1 + q f_2 \quad b_{x2} = -q f_1 + p f_2$$

The quantity b depends therefore only on the accidental value of the amplitude of the electric force on the point where it happens to be, and not on the accidental value of the amplitude of the vibration of the molecule.

$$b_{x1}^2 + b_{x2}^2 = (p^2 + q^2) (f_1^2 + f_2^2) .$$

The amplitude of b_x is therefore $\sqrt{p^2 + q^2}$ times or $4 \pi V^2 e^2$ times

the amplitude of f . Moreover the phasis of b_x is f . As however all phases occur equally frequently the distribution of the quantities $[b_{x1}]$ will be the same as that of the quantities $[f_1]$, so that the chance that b_{x1} is contained within certain limits may be represented by:

$$\frac{1}{\zeta\sqrt{\pi}} e^{-\frac{b_{x1}^2}{\zeta^2}} db_{x1} \quad \text{where } \zeta = 4\pi V^2 e^2 \epsilon^{-1} \text{)}.$$

In order to find the distribution of the vibrations we may reason as follows. Starting from a certain initial condition the molecules will entirely lose their original vibrations by radiation. The vibrations in the direction of the X-axis, which they absorb from the field, are dependent on the f -component of the vibrations of the ether, and not on the g - and h -component. As the f -, g - and h -components are independent of each other, also a_x , a_y and a_z , caused by them, must be independent of each other, and as all directions occur with the same frequency, the distribution of the a 's must also be that of MAXWELL. The chance that the quantity a_{x1} is contained within given limits, may therefore be represented by:

$$\frac{1}{\beta\sqrt{\pi}} e^{-\frac{a_{x1}^2}{\beta^2}} da_{x1}.$$

In order to arrive at this result the solution of the differential equation for a_x is not necessary. In this way however the condition is not yet perfectly determined. From the value found for a_x appears that if a molecule were exposed to an electric wave of constant intensity, it would have assumed the amplitude b after an infinite time. If a molecule is placed in a region where the amplitude of the electric force has a definite value, it will have been for some, though it be a short, time in a region, where the amplitude of the electric force did not differ much from that definite value. So it will have already assumed part of the amplitude b . The probability of the action of a force f on a molecule with a vibration a_x cannot be simply represented by:

$$\frac{1}{\epsilon^2 \pi} e^{-\frac{f_1^2 + f_2^2}{\epsilon^2}} \frac{1}{\beta^2 \pi} e^{-\frac{a_{x1}^2 + a_{x2}^2}{\beta^2}} df_1 df_2 da_{x1} da_{x2},$$

1) Proc. Roy. Acad., Dec. 1899. Pag. 322.

as would be the case if electric force and vibration were independent of each other; but these quantities are dependent on one another. If the above expression held true for the probability of the action, the way of motion would satisfy conditions, exactly corresponding to those which Prof. BOLTZMANN assumes for the case of molecular thermal motion, in order that the motion may be called "molecular-irregulated." ¹⁾ In reality however, the way of motion is here molecular-regulated or as I would call it partially regulated. Totally regulated the condition would be, if the a_{x1} was entirely determined by f ; if e.g. a_{x1} had everywhere assumed the value b_{x1} . The way of motion will be regulated in a higher degree as the quantity

$$\left[\frac{df_1}{dt} = \frac{\partial f_1}{\partial t} + \frac{\partial f_1}{\partial x} \frac{dx}{dt} + \frac{\partial f_1}{\partial y} \frac{dy}{dt} + \frac{\partial f_1}{\partial z} \frac{dz}{dt} \right]$$

is smaller. Here $\frac{\partial f_1}{\partial t}$ represents the fluctuation of f_1 in a point which does not move from its place, $\frac{df_1}{dt}$ the total fluctuation of the quantity f_1 for a molecule which moves with a velocity, the components of which are $\frac{dx}{dt}$, $\frac{dy}{dt}$ and $\frac{dz}{dt}$.

I have however not yet succeeded in finding the law according to which the motion is regulated.

At first sight it may seem strange that the condition of maximum-entropy should possess a certain order, whereas for the case of the molecular thermal motion of a gas we consider the total irregularity as condition for the maximum-entropy. In order to solve this seeming contradiction we must take notice of the fact that we are here concerned with the action of forces. Now we know that the action of external forces which varies so slowly from point to point that they may be thought constant throughout regions which though small, are still measurable and contain many molecules (e.g. gravity), causes the density to be not everywhere the same in the condition of maximum-entropy, so that we have „molar regulation.” But then it is not to be wondered at that the electric forces of radiation, which cannot be thought constant throughout regions of measurable dimensions, should cause a "molecular-regulation".

Even though we had succeeded in determining the regulation in con-

¹⁾ „Molekular-ungeordnet." BOLTZMANN, Gastheorie I. Pag. 21.

sequence of the electric forces, we should not have found the true condition. The influence of the collisions may probably not be neglected. If the mutual collisions of the molecules took place in a perfectly irregular way, they would undoubtedly lessen the degree of regulation, and render the condition nearer irregular. The way of motion is however not only partially regulated with regard to the action of the electric forces on the molecules, but also with regard to the mutual collisions of the molecules. In order to explain this we consider two molecules which have come very near to each other. The forces exercised by the surrounding molecules will be about the same for both, and will tend to bring their internal motion more and more into syntony. Moreover each of the molecules absorbs part of the energy emitted by the other. On account of these two causes a partial regulation is brought about in the collisions of the molecules, of which it seems impossible to me to determine the influence without special hypotheses on the mechanism and even the form of the molecules, for which as yet all data are wanting.

There is however another difficulty which makes me doubt whether the considerations of Prof. BOLTZMANN on the internal motion are applicable to the motion which causes radiation.

For according to Prof. BOLTZMANN the internal energy would increase in proportion to that of the progressive motion of the molecules, i. e. with the temperature. According to the law of STEFAN the emitted energy is proportional to the fourth power of the temperature. These two results can only be brought into harmony by assuming that the absorption decreases strongly with the rise of the temperature.

Properly speaking the law of STEFAN holds good for the total quantity of emitted light and may perhaps only be applied for cases where a continuous spectrum is emitted. The wavelength, which has the greatest intensity depends however for a continuous spectrum on the temperature, so that for the light of a fixed wave-length the law of STEFAN does not hold good. The displacement of the predominating wave-length is however not so great, that the law of STEFAN could not be applied with approximation.

Let us assume that actually the internal energy increases proportional with the temperature, and so the quantity δ^1) with the root of the temperature. Let us represent two temperatures by T_1 and T_2 , the intensities of light emitted at that temperature by I_1 and I_2 and

¹⁾ Proc. Royal Acad. of Sciences, Dec. 1899. Pag. 319.

the corresponding quantities δ and ε by δ_1 and δ_2 and by ε_1 and ε_2 , then we have, neglecting the molecules which surround a point immediately:

$$\frac{T_1^4}{T_2^4} = \frac{I_1}{I_2} = \frac{\varepsilon_1^2}{\varepsilon_2^2} = \frac{\delta_1^2 \int \frac{e^{-2\mu_1 r}}{r^2} \frac{y^2 + z^2}{r^2} d\tau}{\delta_2^2 \int \frac{e^{-2\mu_2 r}}{r^2} \frac{y^2 + z^2}{r^2} d\tau}$$

or

$$\frac{T_1^3}{T_2^3} = \frac{\int \frac{e^{-2\mu_1 r}}{r^2} \frac{y^2 + z^2}{r^2} r^2 dr \sin \varphi d\varphi d\theta}{\int \frac{e^{-2\mu_2 r}}{r^2} \frac{y^2 + z^2}{r^2} r^2 dr \sin \varphi d\varphi d\theta} = \frac{\int_0^\infty e^{-2\mu_1 r} dr}{\int_0^\infty e^{-2\mu_2 r} dr} = \frac{1/\mu_1}{1/\mu_2}$$

Prof. LORENTZ²⁾ has deduced, that μ (his quantity α) is inversely proportional to the root of the temperature. And though both the way in which I have arrived at the conclusion that the absorption is inversely proportional to the third power of the temperature, and that in which Prof. LORENTZ found that it is inversely proportional to the root of the temperature, are but rough approximations yet these results differ too much, to attribute this only to the neglects.

Therefore an incorrect assumption must have been made somewhere. And if so I should doubt in the first place the correctness of the assumption, that for all internal motions the increase of the energy must be proportional to the energy of the progressive motion. I should therefore suppose that in collisions there are influences felt which cause the energy of the internal motions, which bring about radiation, to increase more at a rise of the temperature than the energy of the progressive motion of the molecules.

Mathematics. — “*On rational twisted curves*”. By Prof. P. H. SCHOUTE.

1. Let $P_1, P_2, P_3, P_4, \dots$ be successive points of a given twisted curve R ; then we may consider the centre of circle $P_1 P_2 P_3$ lying in plane $P_1 P_2 P_3$ as well as that of sphere $P_1 P_2 P_3 P_4$. When the

¹⁾ Proc. Royal Acad. of Sciences, Dec. 1899. Png. 322.

²⁾ Versl. Kon. Akad. v. Wet. April 1898, Dl. VI, blz. 559.