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**Physics.** — “*The Entropy of Radiation*”. By J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS.)

The entropy principle may be formulated in different ways. Strictly speaking, nothing follows from the examination of the cyclic process of CARNOT but:

1<sup>st</sup>.  $\int \frac{dQ}{T}$  is a total differential, if the process is reversible.

2<sup>nd</sup>. If we pass from state *A* to state *B* in a not reversible way,  $\int \frac{dQ}{T}$  is smaller than when the process is reversible.

The second formulation is: The entropy tends to a maximum, i. e. the entropy always increases; and if the other conditions to which the system is subjected, allow different processes, that one in which the increase of the entropy is greatest, will take place. As we may consider every slight change as “the process”, we may also say, that the fluctuation of the entropy is always a maximum.

To derive the second formulation from the first, we must generalize the idea entropy. We must then also attribute entropy to substances which are not in equilibrium. It being however impossible, that in a reversible way a substance is brought to a state which is not a state of equilibrium, the definition: entropy is  $\int \frac{dQ}{T}$  for a reversible process, cannot be applied here. It has really been attempted to find a conception of entropy which also applies to substances which are not in a state of equilibrium.

In order that the second formulation of the principle be correct, the original conception must be extended still in another way. An entropy of radiation must be introduced. Whether a deviation from the law of CARNOT might be obtained by radiation, has repeatedly been made the subject of an investigation. BARTOLI <sup>1)</sup> imagined a cycle in which apparently a deviation occurred. Prof. BOLTZMANN <sup>2)</sup> proved however, that this contradiction may be avoided by taking into account the pressure exercised by luminous rays on a body by which they are absorbed or reflected.

In this they tried to solve only this question: Can we obtain by means of radiation a process, in which the substances yield quantities of heat, which have another ratio than would follow from

<sup>1)</sup> BARTOLI, *Sopra i movimenti prodotti dalla luce e dal calore*, FIRENZE, LE MONNIER 1876.

<sup>2)</sup> *Wied. Ann.* XXII 1 Anno 1894. No. 5. Page 31.

the law of CARNOT? WIEN has first introduced an "entropy of radiation" <sup>1)</sup>. He thinks it a matter of course, that radiation which can be in equilibrium with radiating bodies, and which possesses energy, must also possess entropy. He derives his arguments exclusively from the examination of reversible processes. He defines as "temperature of radiation" the temperature of a perfectly black body, which is in equilibrium with this radiation. In reversible processes, however, the quantity of heat yielded by the walls is the same as that communicated to the ether. As further according to the definition the temperatures of the walls and of the radiation are the same, it comes to the same thing whether the law of CARNOT be applied to the ether, as WIEN did, or to the walls, als BOLTZMANN did:  $\int \frac{dQ}{T}$  is identical in both cases. The necessity of the conception "entropy of radiation" can therefore never be concluded from reversible processes.

E. WIEDEMANN had already pointed out the necessity of that conception for phosphorescence- and fluorescence phenomena <sup>2)</sup>.

Yet it is clear that if the entropy principle is expressed in the second formulation, every irreversible radiation phenomenon is in contradiction with the entropy principle, if we do not attribute entropy to radiation. Every body which radiates heat into a vacuum, which heat is not at the same time absorbed by another body, would lose entropy without that at the same time at least an equal amount of entropy was gained elsewhere. Therefore the entropy principle requires, that the ether participating in the movement of radiation, is assumed to have at least as great an amount of entropy, as the radiating body has lost. Whether it is possible to find such an entropy function for radiation, cannot in my opinion, be doubted. This extension of the entropy principle is less hazardous than that in which the second formulation is derived from the first. Yet nobody will doubt whether the second formulation is correct, provided that we follow BOLTZMANN in considering the entropy principle not as an exact law but as a principle of probability.

WIEN derives, inter alia, from his considerations, the theoretical reliability of the law of STEPHAN and the relative intensity of the different wave-lengths in the light emitted by black bodies.

Another advantage of his introduction of the idea of "entropy of

<sup>1)</sup> Wied. Ann. 52,1. Anno 1894. No. 5. P. 132 sequ.

<sup>2)</sup> Wied. Ann. 38,3. Anno 1889. No. 11. P. 485.

radiation" is, that we can ascribe a continuous existence to the entropy: when a body loses entropy by means of radiation and another gains entropy, we need not say, that in one place at least as much is created, as is lost in another place, but that the entropy has moved continuously through space from one place to another. The question about the localization of the entropy is, however, not of so much importance, as that about the localization of the energy. The constancy of this second quantity induces us to think of an identical continuance of existence, so that we postulate a perfectly continuous way of moving. This is not the case with the entropy and as the entropy of a point depends on the condition of the points round it, the entropy of a molecule may be modified by modifying its surroundings, there being no question of a continuous propagation.

For if we assume the formula of BOLTZMANN:

$$H = \int F \log (F) d\omega$$

the amount which every molecule contributes to the entropy is  $-\log(F)$ , as  $-H$  represents the entropy. This quantity is changed momentarily for every molecule of the group  $F$ , when one or more molecules are added to that group, there being no question of propagation. It is remarkable that if the entropy in a volume element increases in consequence of shocks, the amount with which the entropy increases must be ascribed exclusively to the molecules which have collided. For in the quantity  $H$  both  $F$  and  $\log(F)$  change.

The change may be represented by:

$$\int dF \log (F) d\omega + \int F d \log (F) d\omega.$$

The first term is the increase of the entropy of the molecules which have collided, the second term that of the other molecules. The second term, however, appears to be 0, for:

$$\int F d \log (F) d\omega = \int F \frac{1}{F} dF d\omega = \int dF d\omega.$$

This represents the change in the total number of molecules. This number is however, not changed by collisions, and the second term is 0<sup>1)</sup>. If however, the entropy of the volume elements as a whole

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<sup>1)</sup> See BOLTZMANN, Vorlesungen über Gastheorie, 1ste Theil p. 35.

is considered, and not that of every one of the molecules separately, we may say in consequence of the entropy of radiation, introduced by WIEN: the entropy is never lost, and it propagates continuously through space. In what follows I hope to prove: Entropy originates only, when collisions (or their analogue in radiation) occur, and the new entropy is then to be found at that place where the collision has taken place.

Though much might be learned from considerations like those of WIEN, I prefer to make an attempt to obtain an insight into the nature of the entropy of radiation by considerations analogous to those of BOLTZMANN for the entropy of substances.

## II.

When writing the preceding chapter, the treatises of Prof. PLANCK entitled: "Ueber irreversible Strahlungsvorgänge" and his debate with Prof. BOLTZMANN in "Die Sitzungsberichte der Akademie der Wissenschaften zu Berlin, 1897, 1898 and 1899", were unknown to me. My attention was afterwards drawn to them. I found that several of the observations which I have made already occur in Prof. PLANCK's treatises. However, as my opinion differs in many respects from that of Prof. PLANCK, I think that I ought to publish the following paper, though I can oppose against the elaborate system of Prof. PLANCK only a beginning of a system according to my views. To make clear the course of my thoughts, I have left the preceding chapter unchanged. In the first place I shall have to vindicate, why I do not follow the method of treatment of Prof. PLANCK, but follow the considerations of Prof. BOLTZMANN on the molecular thermal movement also for the ethereal movement of radiation. For this purpose I shall put the views of the entropy principle of Prof. BOLTZMANN and Prof. PLANCK in sharp contrast; or at least what seems to me to be the view of Prof. PLANCK, for he does not expressively state his opinion.

Prof. PLANCK's meaning seems to me to be the following:

The basis of his considerations is that the entropy principle is correct, that is to say that the entropy can only increase.

Now many processes which occur in nature, are not elementary e.g. all thermal phenomena can only be treated adequately by applying strict mechanic laws to the separate molecules. In order to find an exact law of nature, it will be necessary to consider an elementary process which is ruled by strict mechanic laws. Now the entropy can change in one direction only, the cause of which

must be found in an elementary process, which can take place in one direction only.

In this way quite a different idea of reversibility is introduced as that which was originally deduced from the cycle of CARNOT. The reversibility according to CARNOT means, if we consider more closely the mechanism of the movement of heat, that all states, through which the system has passed, are states of equilibrium. These states of equilibrium now, are nothing but a particular kind of stationary states, namely such as can exist, without continual change taking place necessarily anywhere outside the system. So e. g. a gas between two plates, one kept at  $100^{\circ}$  by means of steam and the other at  $0^{\circ}$  by means of melting ice, is in a perfectly stationary state, which however is no state of equilibrium, as on one plate steam is continually condensing and on the other ice melting.

It is easy to see that this idea has little in common with the idea of irreversibility of Prof. PLANCK. Many processes are irreversible according to CARNOT, reversible according to Prof. PLANCK, e. g. thermal processes which are brought about by the movement of the molecules. In these processes Prof. PLANCK grants the reversibility according to his definition. As these processes however, increase the entropy, it seems to me, that Prof. PLANCK ought not to have tried to find a process, which is irreversible according to *his* definitions but an explanation, why processes, which are irreversible according to CARNOT can only cause increase of entropy. This observation of mine would seem fallacious only to him who wanted to explain all thermal processes not by molecular motion and collisions, but either by radiation or by an elementary strictly irreversible process of which we have as yet not the least idea. Now we shall investigate the question whether there is really an elementary strictly irreversible process.

Prof. BOLTZMANN denies this positively.

As well in the ordinary mechanics (provided heat and other internal movement be introduced as kinetic energy) as in all ether phenomena no process occurs that could not take place in an opposite direction. If a movement fulfils the equations of LAGRANGE and those of MAXWELL, the same applies to a movement which arises from the former by reversing all velocities and all magnetic forces.

This observation seems to me to be quite decisive. Yet the consideration of all processes is not equally justified. The movement of a HERTZ's vibrator, which is damped because of the emission of radiation, may be thought to take place in opposite direction, so

that a wave converges from the infinite space where it has everywhere the same phasis, exactly into the same point. Yet we are not justified in assuming, that this second movement occurs in nature. On this Prof. PLANCK's considerations are based. He thinks that he has found his perfectly irreversible process in radiation which falls on a resonator. He makes this process really irreversible by excluding a certain number of movements as not occurring. In reality Prof. PLANCK's ideas differ less from those of Prof. BOLTZMANN than he thinks. For the latter calls a great many movements possible, but very improbable, and assumes justly, that such improbable movements may occur both in phenomena of molecular movement and in phenomena of radiation.

Prof. BOLTZMANN's considerations seem to be chiefly as follows. As basis of his considerations he takes the reversibility of all processes, as well mechanical as electrical and magnetical ones. From this follows that a process, in which the entropy increases, might also take place in the opposite direction, so that the entropy decreased. Apparently this is in contradiction with the experiment which teaches us, that only those processes occur, in which the entropy increases. To explain this apparent contradiction, Prof. BOLTZMANN argues as follows:

If we know exactly the initial conditions of a system with  $n$  degrees of freedom, i.e. the  $n$  generalised coordinates and their fluctuations at a given moment, and if we know the laws of all the forces, acting on the system, we can calculate the state of the system at any moment. If however we know at a given moment only  $n - 1$  of the coordinates and their fluctuations, we can in general calculate nothing for a later moment. The want of knowledge of one of the  $2n$  necessary data, makes not only that one coordinate indetermined for the future, but all the coordinates. If we consider a gas as a system with many degrees of freedom, the condition would be exactly determined only then, if at a given moment we know exactly the coordinates and their fluctuations for every molecule separately. As we however never know them, we can never say how the condition in the next moment will be. Perfectly general laws for movement of heat can therefore not be drawn up.

By varying the coordinates of the separate molecules, we can however obtain a great number of systems, all of which fulfil the conditions, which are required to call the system in question a gas or a solid substance with a certain temperature and under a certain pressure and which differ only in the coordinates of the separate molecules. The number of these systems is infinite. Now Prof.

BOLTZMANN has proved that for the vast majority of those systems, the state after a given time is of course not perfectly determined, but yet fulfils certain conditions, that namely the mean density and the mean kinetic energy in every volume element will be such that we may speak again of a solid or a gas of a certain temperature and under a certain pressure. Of course this is not proved for the great majority of all systems *occurring in nature*, but for all *imaginable* systems which answer to our idea "substance of a certain temperature and under a certain pressure". If we suppose all these different systems to be equally probable, we may say that it is highly improbable that we meet with a phenomenon, in which the entropy increases with a measurable amount. The supposition of Prof. BOLTZMANN that these systems are equally probable, is not new. Every one who has written on kinetic gas theory could not but make this supposition though in a somewhat different formulation, in order to calculate the mean number of collisions and such like quantities. The fact that observations show that the entropy always increases, justifies the assumption that this supposition agrees with reality. Convinced of the correctness of these considerations of Prof. BOLTZMANN, I wanted to treat the entropy of radiation in a similar way. The  $H$  theorem of Prof. BOLTZMANN is closely connected with the distribution of velocities according to MAXWELL. Therefore I thought that I had in the first place to find the analogue of it for the distribution of the electric forces in a space, in which a great number of radiating molecules are to be found. This distribution will be treated in the following chapter.

First some observations on an, in my opinion, essential consequence of the considerations of Prof. BOLTZMANN, viz that the entropy increases only in consequence of collisions.

To show this we take the following process into consideration:

The walls inclosing a quantity of gas are suddenly removed at the moment  $t$ , so that the gas spreads in an infinite vacuum. We leave the molecular attraction out of account. If we take the gas at a high degree of rarefaction and if the volume in which it was enclosed is supposed to be not too large, many molecules will move away without any collision. In order that we may apply BOLTZMANN'S  $H$  theorem, we must have a large quantity of molecules. The assumption that after the moment  $t$  not a single molecule collides, may be in opposition to this requirement. Yet we may examine what might be the consequence of the assumption that all molecules moved away with the velocity which they had at the moment



$t$ , without changing it by collisions. It is easy to show, that the entropy would then remain constant.

Let us first think the gas enclosed in a small cube with a centre  $O$ , the axes being taken parallel to the sides. We get

$$H = \iiint \iiint \iiint F \log (F) dx dy dz d\xi d\eta d\zeta$$

$\xi \eta \zeta$  representing the components of the velocities of the molecules. The first three integrals for  $x y$  and  $z$  must be taken between the limits  $-\frac{1}{2}a$  and  $+\frac{1}{2}a$ , where  $a$  represents the edge of the cube, and the other three for  $\xi \eta$  and  $\zeta$  between  $-\infty$  and  $+\infty$ . If the volume of the cube was 0, the velocity of the molecules which had reached after one second the point  $P(x' y' z')$  at a distance  $r$  from  $O$  would also be  $r$  and their density  $a^3 F(x' y' z')$ .

By assuming this density as being the real one, we shall make a slight error. For the velocity we must however take into account that the velocity of molecules, which reach  $P$  after one second, starting from different points of the cube, is different.

The probability that the components of the velocity of a molecule which has reached point  $P$ , are enclosed between the limits:

$$x' + x = \xi' \text{ and } x' + x + dx = \xi' + d\xi'$$

$$y' + y = \eta' \text{ and } y' + y + dy = \eta' + d\eta'$$

$$z' + z = \zeta' \text{ and } z' + z + dz = \zeta' + d\zeta'$$

$x, y$  and  $z$  representing the coordinates of the point of the cube, from which the molecule has started, is:

$$\frac{dx dy dz}{a^3} = \frac{d\xi' d\eta' d\zeta'}{a^3}$$

we find for  $H$  after one second:

$$\begin{aligned} H' &= \iiint \iiint \iiint a^3 F' \frac{1}{a^3} \log \left( a^3 F' \frac{1}{a^3} \right) dx' dy' dz' d\xi' d\eta' d\zeta' \\ &= \iiint \iiint \iiint F' \log (F') dx' dy' dz' d\xi' d\eta' d\zeta' \end{aligned}$$

$F'$  is obtained, as we have seen, by substituting  $r$  in  $F$  for the velocity;  $r$  represents the distance from an arbitrary point to the origin.

The integrals with respect to  $x$ ,  $y$  and  $z$  must here be taken between  $-\infty$  en  $+\infty$ , those with respect to  $\xi$ ,  $\eta$  and  $\zeta$  between  $-\frac{1}{2}a$  and  $+\frac{1}{2}a$ . Therefore  $H'$  is equal to  $H$ , the only difference is that the coordinates have been interchanged with the velocities. The unity of time being arbitrary  $H$  will remain also constant after an arbitrary time.  $H$  changes only if the molecules which are moving away, cannot reach infinity, but come in collision with a new wall and are arranging themselves into a state of stationary movement in the new volume.

The great importance which I think ought to be attached to the collisions, made me look for its analogue in radiation. For this purpose I have had to make a supposition on the nature of radiating molecules. I have namely imagined them as HERTZ's vibrators all of the same period. In this case the emitted radiation also has everywhere the same period. Its amplitude varies from point to point and changes with the time. As collision of a special kind I consider the action of an alternating electric force of a determinate direction, intensity, and phasis on a molecule, which is in a vibration, the direction, amplitude and phasis of which are also determinate. According to this, every molecule is always in collision.

This view agrees with an observation of Prof. PLANCK, who says more generally <sup>1)</sup>:

„Durch die Strahlungsvorgänge im freien Felde kann also keine Entropieänderung des Systems hervor gerufen werden. Dagegen bewirkt jeder Resonator im allgemeinen eine Entropieänderung der ihm treffenden Strahlenbündel.“

### III.

#### *Law of the distribution of Electrical forces.*

Concerning the nature of radiating molecules there are principally two conceptions. The first is that a source of light has a periodical movement, which gives rise to more or less regular vibrations in the ether. The other conception is that the molecules bring about perfectly irregular disturbances of the ether, which get a seeming periodicity from the apparatus by means of which we observe. Possibly both these suppositions are partly true and in some sources

<sup>1)</sup> Berliner Sitzungsberichte XXV 18 Mai 1899 pag. 467.

of light the regular, in others the irregular ways of movement are more prominent. As my considerations will be simplest for a gas, and we are there most inclined to think of vibrations in the molecules, I have chosen the first conception; and that in very simplified suppositions, hoping that these may be extended for processes such as really occur in nature. I imagine namely a great number of molecules spread in space which I suppose as vibrating, all with exactly the same period. I leave out of account the change of the period caused by the DOPPLER effect. I suppose that for those molecules vibrations in the direction of the  $x$ ,  $y$  and  $z$ -axis are on an average equally represented, while also all phases equally probable.

These suppositions are sufficient for finding something about the distribution of the forces, without our having to determine whether or no all molecules have the same amplitude; and if not, how the distribution of the amplitudes will be.

Let us now consider a volume element  $d\tau$ . The action of it at a certain distance will be only determined by its electrical moment and the way in which that changes, and not by the way in which that moment is spread over the element.

If the moments of the molecules now had the most probable distribution, i. e. if all directions and phases were exactly equally represented, the moment of the element would be always 0 and no radiation would take place. The most probable distribution, however, is itself highly improbable, and generally a deviation will be found. This deviation is the cause of radiation. Let us assume that the unity of volume contains  $n$  molecules. Let us represent the components of their vibration by:

$$a_x = a_{x1} \cos. \frac{2\pi t}{T} + a_{x2} \sin. \frac{2\pi t}{T}$$

$$a_y = a_{y1} \cos. \frac{2\pi t}{T} + a_{y2} \sin. \frac{2\pi t}{T}$$

$$a_z = a_{z1} \cos. \frac{2\pi t}{T} + a_{z2} \sin. \frac{2\pi t}{T}$$

and let us call the number of the molecules per unity of volume, the amplitudes of which are contained between the limits:

$a_{x1}$ ,  $a_{x2}$ ,  $a_{y1}$ ,  $a_{y2}$ ,  $a_{z1}$  and  $a_{z2}$  and

$da_{x1}$ ,  $da_{x2}$ ,  $da_{y1}$ ,  $da_{y2}$ ,  $da_{z1}$  and  $da_{z2}$ ,

$F(a_{x1} a_{x2} a_{y1} a_{y2} a_{z1} a_{z2}) da_{x1} da_{x2} da_{y1} da_{y2} da_{z1} da_{z2}$  or  $F d\omega$ .

The group, the amplitudes of which have the same values, but all the opposite sign, will be about as numerous. These two groups together contain  $\pm 2F d\omega$  molecules. If the most probable distribution prevailed, these two groups would have exactly the same number of molecules and would furnish together a moment 0.

If we have an event, which may take place in two directions, the probability for one direction being  $p$  and that for the other  $q$  (where  $p + q = 1$ ) and if this event occurs a very great number ( $n$ ) of times, the calculus of probabilities teaches that the chance, that of these  $n$  events the number which occurs in one direction is between  $np + \nu$  and  $np + \nu + d\nu$ , is represented by:

$$\frac{1}{C\sqrt{\pi}} e^{-\frac{\nu^2}{C^2}} d\nu.$$

In this  $C$  is equal to  $\sqrt{2npq}$  and is called modulus.

If we apply this to the  $2F d\omega d\tau$  molecules, then  $p = q = \frac{1}{2}$ .

The probability that the deviation, which one of the groups shows from the most probable value, lies between  $\nu$  and  $\nu + d\nu$ , is:

$$\frac{1}{\beta\sqrt{\pi}} e^{-\frac{\nu^2}{\beta^2}} d\nu$$

where  $\beta = \sqrt{F d\omega d\tau}$ .

Of the  $2F d\omega$  molecules one group has a deviation of  $+\nu$ , so that it amounts to  $F d\omega + \nu$ , the other group has a deviation of  $-\nu$  and amounts to  $F d\omega - \nu$ . The difference between the two groups is then  $2\nu$  and the amount they contribute to the moment of the volume element is  $[2\nu a_{x1}]$ .

If we put:

$$[2\nu a_{x1} = m_{x1}]$$

in which the brackets indicate that also a corresponding expression for the  $y$  and  $z$  components and for the coefficients of  $\sin \frac{2\pi t}{T}$  is meant, then we may represent the probability that the two groups in consideration contribute to the moment of the volume element an amount, the amplitudes of which lie between

$$[m_{x1}] \text{ and } [m_{x1} + dm_{x1}]$$

by

$$\frac{1}{\gamma\sqrt{\pi}} e^{-\frac{m_{x1}^2}{\gamma^2}} dm_{x1}$$

where

$$\gamma = 2 a_{x1} \beta.$$

Now we are going to seek the probability that the total moment  $M$  of the volume element i. e., the sum of the amounts contributed by the separately considered groups of molecules, has amplitudes which lie between:

$$[M_{x1}] \text{ and } [M_{x1} + dM_{x1}].$$

According to the calculus of probabilities the probability for such a sum is again represented by a function of the same form as the separate terms, while the modulus is the root of the sum of the squares of the moduli of the separate terms. So:

$$\delta = \sqrt{\frac{1}{2} \iiiii \iiiii 4a_{x1}^2 F d\omega d\tau.}$$

If we take the integrals between the limits  $-\infty$  and  $+\infty$ , the factor  $\frac{1}{2}$  must not be omitted, because we have to take only half of all the groups: for if we take a group with definite amplitudes, that one with equal amplitudes, but of opposite sign has been taken into account at the same time.

For the other quantities  $M_{x2}$ ,  $M_{y1}$ ,  $M_{y2}$ ,  $M_{z1}$  and  $M_{z2}$  of course the same formula holds good. Now we have still to prove that the chances for these quantities are independent of one another. To this purpose we draw vectors from point  $O$ , which have the quantities  $M_{x1}$ ,  $M_{y1}$  and  $M_{z1}$  as components. Along the axes the density of the final points of these vectors is the same as in the distribution of velocities of MAXWELL. If a large  $M_{y1}$  was probably accompanied by a large  $M_{x1}$ , the distribution in space would not be that of MAXWELL. The choice of the axis is however perfectly arbitrary, and the distribution along every line passing through  $O$ , must be the same as along the  $x$ -axis. From this follows that the distribution is really the same, as that which MAXWELL found for the velocities, i. e. that the chances of the quantities  $M_{x1}$ ,  $M_{y1}$  and  $M_{z1}$  are independent of each other. In a corresponding way we may prove this for  $M_{x1}$  en  $M_{x2}$ ,  $M_{y1}$  and  $M_{y2}$ ,  $M_{z1}$  and  $M_{z2}$ .

If we represent the mean of the squares of all quantities  $a_{x1}$  by  $\overline{a_{x1}^2}$ , we get:

$$\delta = \sqrt{2n} \cdot \sqrt{\overline{a_{x1}^2}}$$

and

$$\overline{M_{z1}^2} = n \overline{a_z^2}$$

The electric and the magnetic forces of the ether vibrations, emitted by the element are proportionate to  $[M_{z1}]$ . The emitted energy is therefore proportionate to  $\overline{[M_{z1}^2]}$ . This energy proves to be on an average the sum of the quantities of the energy, which every molecule would emit, if it were alone in space.

Let us now examine what would be the distribution of the electric and the magnetic forces, the components of which we represent by:

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

$$g = g_1 \cos. \frac{2\pi t}{T} + g_2 \sin. \frac{2\pi t}{T}$$

$$h = h_1 \cos. \frac{2\pi t}{T} + h_2 \sin. \frac{2\pi t}{T}$$

$$L = L_1 \cos. \frac{2\pi t}{T} + L_2 \sin. \frac{2\pi t}{T}$$

$$M = M_1 \cos. \frac{2\pi t}{T} + M_2 \sin. \frac{2\pi t}{T}$$

$$N = N_1 \cos. \frac{2\pi t}{T} + N_2 \sin. \frac{2\pi t}{T}$$

For this we apply the following formula <sup>1)</sup>:

$$f = -V^2 \left\{ \frac{\partial^2 \chi_x}{\partial x^2} + \frac{\partial^2 \chi_y}{\partial x \partial y} + \frac{\partial^2 \chi_z}{\partial x \partial z} \right\} + \frac{\partial^2 \chi}{\partial t^2}$$

and

$$L = 4\pi V^2 \left\{ \frac{\partial^2 \chi_y}{\partial z \partial t} - \frac{\partial^2 \chi_z}{\partial y \partial t} \right\}$$

$$\chi_x = -\frac{1}{4\pi V^2} \int \frac{M_x}{r} d\tau, \quad \chi_y = -\frac{1}{4\pi V^2} \int \frac{M_y}{r} d\tau, \quad \chi_z = -\frac{1}{4\pi V^2} \int \frac{M_z}{r} d\tau$$

where  $M$  represents the moment of a volume-element at the moment  $t - \frac{r}{V}$ , so that:

<sup>1)</sup> LORENTZ Arch. Neerl. XXV 5. 1892 pag. 429.

$$\chi_x = -\frac{1}{4\pi V} \int \frac{1}{r} \left\{ M_{x1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{x2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} dr$$

and  $f = \frac{1}{4\pi} \int \left[ \frac{\partial^2}{\partial x^2} \frac{1}{r} \left\{ M_{x1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{x2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} + \right.$

$$+ \frac{\partial^2}{\partial x \partial y} \frac{1}{r} \left\{ M_{y1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{y2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} +$$

$$+ \frac{\partial^2}{\partial x \partial z} \frac{1}{r} \left\{ M_{z1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{z2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} -$$

$$\left. - \frac{1}{V^2} \frac{\partial^2}{\partial t^2} \frac{1}{r} \left\{ M_{x1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{x2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} \right] dr$$

In this the influence of absorption has been neglected. In a complete theory we should have to calculate it by examining to what influence the vibration of every molecule is subjected by the radiation of every other molecule. Then it would be necessary to take into account the influence of the damping, which the vibrating molecules experience, and the quite unknown influence of the collisions. Here I shall confine myself to assume that the disturbances, when they have propagated over the unity of length, are reduced to  $e^{-\mu}$  of their original amount. Then we have to multiply with  $e^{-\mu r}$  every term under the integral sign in the expression for  $f$ .

For points for which  $r$  is great compared with the wave length, we may write by approximation:

$$f = -\frac{1}{4\pi} \left( \frac{2\pi}{TV} \right)^2 \int \frac{e^{-\mu r}}{r} \left[ \left\{ M_{x1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{x2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} \frac{x^2}{r^3} + \right.$$

$$+ \left\{ M_{y1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{y2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} \frac{xy}{r^3} +$$

$$+ \left\{ M_{z1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{z2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} \frac{xz}{r^3} -$$

$$\left. - \left\{ M_{x1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{x2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} \right] dr.$$

So the modulus for the probability, that  $[f_1]$  lies between the limits  $[f_1]$  and  $[f_1 + df_1]$ , becomes:

$$\begin{aligned} \varepsilon &= \frac{1}{4\pi} \left( \frac{2\pi}{TV} \right)^2 \delta \sqrt{\int \frac{e^{-2\mu r}}{r^2} \left\{ \left( \frac{y^2 + z^2}{r^2} \right)^2 + \left( \frac{xy}{r^2} \right)^2 + \left( \frac{xz}{r^2} \right)^2 \right\} dr} \\ &= \frac{\pi}{\lambda^2} \delta \sqrt{\int \frac{e^{-2\mu r}}{r^2} \frac{y^2 + z^2}{r^2} dr.} \end{aligned}$$

In the same way we find for  $L$ :

$$\begin{aligned} L &= - \int e^{-\mu r} \left\{ \frac{\partial^2}{\partial y \partial t} \frac{1}{r} \left\{ M_{z1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{z2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} \right. \\ &\quad \left. - \frac{\partial^2}{\partial z \partial t} \frac{1}{r} \left\{ M_{y1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{y2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} \right\} dr \end{aligned}$$

or by approximation:

$$\begin{aligned} L &= - \frac{2\pi}{T} \frac{2\pi}{TV} \int \frac{e^{-\mu r}}{r} \left[ \frac{y}{r} \left\{ M_{z1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{z2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} \right. \\ &\quad \left. - \frac{z}{r} \left\{ M_{y1} \cos \frac{2\pi}{T} \left( t - \frac{r}{V} \right) + M_{y2} \sin \frac{2\pi}{T} \left( t - \frac{r}{V} \right) \right\} \right] dr \end{aligned}$$

and for the modulus of the corresponding chance:

$$\eta = \left( \frac{2\pi}{T} \right)^2 \frac{1}{V} \delta \sqrt{\int \frac{e^{-2\mu r}}{r^2} \frac{y^2 + z^2}{r^2} dr.}$$

The reasoning, according to which these formulae have been derived, is correct only when we may choose volume elements, which contain many molecules and which are yet small compared with a wave-length and with  $r$ . It does not hold for the immediate surroundings of a point. Yet the not approximated formulae for  $[f_1]$  and  $[L_1]$  hold also for the immediate surroundings, provided we neglect the volume of the molecules. If we imagine an element  $dx dy dz$  or  $dr$  at the distance  $r$  from the point  $P$ , then the probability that we should find a molecule in it, is  $n dr$ . The chance, that we should find a molecule in it with  $a_{x1}$  lying between  $a_{x1}$  and  $a_{x1} + da_{x1}$ , is  $F_1(a_{x1}) da_{x1} n dr$ .

If we imagine a region  $\Delta x \Delta y \Delta z$ , which contains many ( $p$ ) elements  $dr$  and which is yet small compared with the wave-length and  $r$ , then the chance, that this region has a moment  $[M_{x1}]$  is the sum of the chances of the different ways, in which that moment



may be brought about. The chance, that the volume element  $d\tau$  contains no molecule is the chance, that all the  $n$  molecules of the unity of volume lie outside the element. For one molecule this chance is  $1 - d\tau$ , so for the  $n$  molecules  $(1 - d\tau)^n$ . Now the moment  $M_{x1}$  may be brought about by the fact that in  $q$  elements  $d\tau$  we have no molecule, in  $p - q - 1$  we have a molecule, every one of which has an arbitrary amplitude  $a_{x1}$  and in the last element with the amplitude  $p a_{x1} = M_{x1} - \sum a_{x1}$ . The chance of being brought about in this way, is:

$$(1 - d\tau)^{nq} (nd\tau)^{p-q} F_1(a_{x1}) F_1(2a_{x1}) \dots F_1(p - q - a_{x1}) F_1(M_{x1} - \sum a_{x1}) \\ d(a_{x1}) d(2a_{x1}) \dots d(p - q - a_{x1}) dM_{x1}.$$

We find the total change for an amplitude between  $M_{x1}$  and  $M_{x1} + dM_{x1}$  by first integrating with respect to  $1a_{x1}, 2a_{x1} \dots p - q - 1 a_{x1}$  between the limits  $-\infty$  and  $+\infty$ , and by adding the results for all values of  $q$ .

As we have to do this for the case in which  $p = \infty$ , we execute this addition by multiplying with  $dq$  and by then integrating with respect to  $q$  between the limits 0 and  $\infty$ . These formulae hold always, independent of the size of  $\Delta x \Delta y \Delta z$ , and as we have found for it for a region with many molecules

$$\frac{1}{\delta \sqrt{\pi}} e^{-\frac{M_{x1}^2}{\delta^2}} \text{ where } \delta = \sqrt{\frac{1}{2}} n \Delta x \Delta y \Delta z.$$

this formula will also hold if  $\Delta x \Delta y \Delta z$  is so small that the chance that it contains a molecule, is slight.

In this we have assumed, that the fact, that at a certain point  $P$  a definite moment  $[M_{x1}]$  prevails, has no influence on the chance for the moment of the immediately surrounding points. This would be true only if the molecules themselves had no extension. If however point  $P$  lies in a molecule, which has extension, the surrounding points will also have moments of the same direction and the same phasis as  $P$ . If this circumstance however, causes a deviation from the here derived law of probability, it will probably be very small for gases.

Our result shows that in the unity of volume the total region in which  $f_1$  is contained between the limits  $f_1$  and  $f_1 + df_1$  is:

$$\frac{1}{\varepsilon \sqrt{\pi}} - \frac{f_1^2}{\varepsilon^3} df_1$$

and that the changes for  $f_1, f_2, g_1, g_2, h_1$  and  $h_2$  are independent of one another.

This does not completely determine the condition: it is left unsettled, how the total region is spread over the unity of volume; whether it probably consists of comparatively few regions which are not so very small, or of a great many very small regions. In order to find something about this, we should have to calculate the probable value of  $\left[ \frac{\partial f_1}{\partial x} \right]$ . In the same way we might also try to find

the probable value of  $\left[ \frac{\partial f_1}{\partial t} \right]$ . Whereas  $\left[ \frac{\partial f_1}{\partial x} \right]$  may be deduced from the suppositions which we have already made, new suppositions would be necessary, in order to find  $\left[ \frac{\partial f_1}{\partial t} \right]$ . It would be namely necessary, to make suppositions about the causes of change of  $[a_{x1}]$ . The significance of these quantities will appear from the following chapter.

At first I had thought that the name "entropy of the ether" would be preferable to that of "entropy of radiation." The name introduced by WIEN "entropy of radiation," seems however, preferable to me. At the absolute zeropoint matter has an entropy  $-\infty$ . Now both the formulae, that of WIEN and that of PLANCK, give for space without radiation 0 as the quantity of entropy; and this result seems correct to me. In order to maintain the analogy between the two kinds of entropy, it seems best to me, to ascribe the entropy not to the ether but to the radiation. A space, where no radiation takes place, can consequently not contain entropy of radiation.

If we speak of entropy of the ether, it would probably have a form like the following:

$$\int F([f_1]) \log F[df_1].$$

Probably however the entropy will be represented by a form like the following:

$$\int \varphi([f_1]) F([f_1]) \log(\varphi F) \cdot [df_1]$$

in which  $\varphi$  represents the density, i.e. it has the same function as  $n$  in the formula of BOLTZMANN:

$$H = \int F \log (F) d\omega \quad \text{where: } F = \frac{n}{\alpha\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}}$$

Possibly this  $\varphi$  is nothing but the energy per unity of volume, which quantity we are most inclined to call "density of radiation."

For the distribution of the magnetic forces the entropy will consist of another term formed in a similar way. Possibly however we shall have to find the entropy not from the electric and the magnetic forces separately, but from the vectors of POYNTING.

We find therefore the analogue of matter at the absolute 0-point not in a space without radiation, but in absolutely regular movement, e.g. in a plain wave of monochromatic light, everywhere with the same amplitude. Let us represent this wave by:

$$f = f_0 \cos. \frac{2\pi}{T} \left( t - \frac{y}{V} \right),$$

$$g = 0, \quad h = 0.$$

Here we must take into consideration, that in this case  $f_1$  and  $f_2$  are not independent of each other, so that we cannot simply add the entropy for these two terms. Probably we have to diminish the amplitude everywhere with:

$$f_0 \cos. \frac{2\pi y}{\lambda} \text{ and } f_0 \sin. \frac{2\pi y}{\lambda}$$

and we have to take for  $F$  the chance that the remaining amplitude lies between certain limits, i.e.

$$F = \frac{1}{c\sqrt{\pi}} e^{-\frac{f_1'^2}{c^2}} \text{ where } c = 0 \text{ and } f_1' = f_1 - f_0 \cos. \frac{2\pi y}{\lambda}.$$

This is analogous to the way, in which we prove for a gas of  $0^\circ$ , which moves as a whole, that the quantity  $H$  of BOLTZMANN becomes  $\infty$ .

If we put for  $\varphi$  the mean energy, we find:

$$H = \int_{-\infty}^{+\infty} f_1'^2 \frac{1}{c\sqrt{\pi}} e^{-\frac{f_1'^2}{c^2}} \left\{ -lc - \frac{1}{2} l\pi - \frac{f_1'^2}{c^2} \right\} df_1' = \infty$$

So the entropy is  $-\infty$ .