Physics. — *"The absorption and emission lines of gaseous bodies."* By Prof. H. A. LORENTZ.

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§ 1. The dispersion and absorption of light, as well as the influence of certain circumstances on the bands or lines of absorption, can be explained by means of the hypothesis that the molecules of ponderable bodies contain small particles that are set in vibration by the periodic forces existing in a beam of light or radiant heat. The connexion between the two first mentioned phenomena forms the subject of the theory of anomalous dispersion that has been developed by SELLMEYER, BOUSSINESQ and HELMHOLTZ, a theory that may readily be reproduced in the language of electromagnetic theory, if the small vibrating particles are supposed to have electric charges, so that they may be called electrons. Among the changes in the lines of absorption, those that are produced by an exterior magnetic field are of paramount interest. VOIGT [1]) has proposed a theory which not only accounts for these modifications, the inverse ZEEMAN effect as it may properly be called, but from which he has been able to deduce the existence of several other phenomena, which are closely allied to the magnetic splitting of spectral lines, and which have been investigated by HALLO [2]) and GEEST [3]) in the Amsterdam laboratory. In this theory of VOIGT there is hardly any question of the mechanism by which the phenomena are produced. I have shown however that equations corresponding to his and from which the same conclusions may be drawn, may be established on the basis of the theory of electrons, if we confine ourselves to the simpler cases. In what follows I shall give some further development to my former considerations on the subject, somewhat simplifying them at the same time by the introduction of the notation I have used in my articles in the Mathematical Encyclopedia.

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1) W. VOIGT, Theorie der magneto-optischen Erscheinungen. Ann. Phys. Chem. **67** (1899), p. 345; Weiteres zur Theorie des ZEEMAN-effectes, ibidem **68** (1899), p. 352; Weiteres zur Theorie der magneto-optischen Wirkungen. Ann. Phys., **1** (1900), p. 389.

2) J. J. HALLO, La rotation magnétique du plan de polarisation dans le voisinage d'une bande d'absorption, Arch. Néerl, (2), **10** (1905), p. 148.

3) J. GEEST, La double réfraction magnétique de la vapeur de sodium, Arch. Néerl., (2), **10** (1905), p. 291.

4) LORENTZ, Sur la théorie des phénomènes magnéto-optiques récemment découverts Rapports prés. au Congrès de physique, 1900, T. **3**, p. 1.

§ 2. We shall always consider a gaseous body. Let, in any point of it, $\mathfrak{E}$ be the electric force, $\mathfrak{H}$ the magnetic force, $\mathfrak{P}$ the electric polarization and

$$\mathfrak{D} = \mathfrak{E} + \mathfrak{P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the dielectric displacement. Then we have the general relations

$$\frac{\partial \mathfrak{H}_z}{\partial y} - \frac{\partial \mathfrak{H}_y}{\partial z} = \frac{1}{c}\frac{\partial \mathfrak{D}_x}{\partial t}, \quad \frac{\partial \mathfrak{H}_x}{\partial z} - \frac{\partial \mathfrak{H}_z}{\partial x} = \frac{1}{c}\frac{\partial \mathfrak{D}_y}{\partial t},$$

$$\frac{\partial \mathfrak{H}_y}{\partial x} - \frac{\partial \mathfrak{H}_x}{\partial y} = \frac{1}{c}\frac{\partial \mathfrak{D}_z}{\partial t}, \quad . \quad . \quad (2)$$

$$\frac{\partial \mathfrak{E}_z}{\partial y} - \frac{\partial \mathfrak{E}_y}{\partial z} = -\frac{1}{c}\frac{\partial \mathfrak{H}_x}{\partial t}, \quad \frac{\partial \mathfrak{E}_x}{\partial z} - \frac{\partial \mathfrak{E}_z}{\partial x} = -\frac{1}{c}\frac{\partial \mathfrak{H}_y}{\partial t},$$

$$\frac{\partial \mathfrak{E}_y}{\partial x} - \frac{\partial \mathfrak{E}_x}{\partial y} = -\frac{1}{c}\frac{\partial \mathfrak{H}_z}{\partial t}, \quad . \quad . \quad (3)$$

in which c is the velocity of light in the aether.

To these we must add the formulae expressing the connexion between $\mathfrak{E}$ and $\mathfrak{P}$, which we can find by starting from the equations of motion for the vibrating electrons. For the sake of simplicity we shall suppose each molecule to contain only one movable electron. We shall write $\mathbf{e}$ for its charge, m for its mass and $(\mathbf{x}, \mathbf{y}, \mathbf{z})$ for its displacement from the position of equilibrium. Then, if N is the number of molecules per unit volume,

$$\mathfrak{P}_x = N\mathbf{e}\mathbf{x}, \quad \mathfrak{P}_y = N\mathbf{e}\mathbf{y}, \quad \mathfrak{P}_z = N\mathbf{e}\mathbf{z}. \quad . \quad . \quad . \quad . \quad (4)$$

§ 3. The movable electron is acted on by several forces. First, in virtue of the state of all other molecules, except the one to which it belongs, there is a force whose components per unit charge are given by [1])

$$\mathfrak{E}_x + \alpha\mathfrak{P}_x, \quad \mathfrak{E}_y + \alpha\mathfrak{P}_y, \quad \mathfrak{E}_z + \alpha\mathfrak{P}_z,$$

α being a constant that may be shown to have the value $^1/_3$ in certain simple cases and which in general will not be widely different from this. The components of the first force acting on the electron are therefore

$$\mathbf{e}(\mathfrak{E}_x + \alpha\mathfrak{P}_x), \quad \mathbf{e}(\mathfrak{E}_y + \alpha\mathfrak{P}_y), \quad \mathbf{e}(\mathfrak{E}_z + \alpha\mathfrak{P}_z) \quad . \quad . \quad . \quad (5)$$

In the second place we shall assume the existence of an elastic force directed towards the position of equilibrium and proportional to the displacement. We may write for its components

$$-f\mathbf{x}, \quad -f\mathbf{y}, \quad -f\mathbf{z}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

f being a constant whose value depends on the nature of the molecule.

[1]) Lorentz, Math. Encycl. Bd. 5, Art. 14, §§ 35 and 36.

If this were the only force, the electron could vibrate with a frequency n_0, determined by

$$n_0^2 = \frac{f}{m} \quad \ldots\ldots\ldots\ldots \quad (7)$$

In order to account for the absorption, one has often introduced a resistance proportional to the velocity of the electron whose components may be represented by

$$-g\frac{d\mathbf{x}}{dt}, \quad -g\frac{d\mathbf{y}}{dt}, \quad -g\frac{d\mathbf{z}}{dt}, \quad \ldots\ldots \quad (8)$$

if by g we denote a new constant.

We have finally to consider the forces due to the external magnetic field. We shall suppose this field to be constant and to have the direction of the axis of z. If the strength of the field is $\mathbf{H}$, the components of the last mentioned force will be

$$\frac{\mathbf{eH}}{c}\frac{d\mathbf{y}}{dt}, \quad -\frac{\mathbf{eH}}{c}\frac{d\mathbf{x}}{dt}, \quad 0 \quad \ldots\ldots\ldots \quad (9)$$

It must be observed that, in the formulae (2) and (3), we may understand by $\mathfrak{H}$ the magnetic force that is due to the vibrations in the beam of light and that may be conceived to be superimposed on the constant magnetic force $\mathbf{H}$.

§ 4. The equations of motion of the electron are

$$m\frac{d^2\mathbf{x}}{dt^2} = \mathbf{e}(\mathfrak{E}_x + \alpha\mathfrak{P}_x) - f\mathbf{x} - g\frac{d\mathbf{x}}{dt} + \frac{\mathbf{eH}}{c}\frac{d\mathbf{y}}{dt},$$

$$m\frac{d^2\mathbf{y}}{dt^2} = \mathbf{e}(\mathfrak{E}_y + \alpha\mathfrak{P}_y) - f\mathbf{y} - g\frac{d\mathbf{y}}{dt} - \frac{\mathbf{eH}}{c}\frac{d\mathbf{x}}{dt},$$

$$m\frac{d^2\mathbf{z}}{dt^2} = \mathbf{e}(\mathfrak{E}_z + \alpha\mathfrak{P}_z) - f\mathbf{z} - g\frac{d\mathbf{z}}{dt}.$$

These formulae may however be put in a form somewhat more convenient for our purpose.

To this effect we shall divide by $\mathbf{e}$, expressing at the same time $\mathbf{x}, \mathbf{y}, \mathbf{z}$ in $\mathfrak{P}_x, \mathfrak{P}_y, \mathfrak{P}_z$. This may be done by means of the relations (4).

Putting

$$\frac{m}{N\mathbf{e}^2} = m', \quad \frac{f}{N\mathbf{e}^2} = f', \quad \frac{g}{N\mathbf{e}^2} = g', \quad \ldots\ldots \quad (10)$$

we find in this way

$$m'\frac{\partial^2\mathfrak{P}_x}{\partial t^2} = \mathfrak{E}_x + \alpha\mathfrak{P}_x - f'\mathfrak{P}_x - g'\frac{\partial\mathfrak{P}_x}{\partial t} + \frac{\mathbf{H}}{cN\mathbf{e}}\frac{\partial\mathfrak{P}_y}{\partial t},$$

$$m'\frac{\partial^2\mathfrak{P}_y}{\partial t^2} = \mathfrak{E}_y + \alpha\mathfrak{P}_y - f'\mathfrak{P}_y - g'\frac{\partial\mathfrak{P}_y}{\partial t} - \frac{\mathbf{H}}{cN\mathbf{e}}\frac{\partial\mathfrak{P}_x}{\partial t},$$

$$m'\frac{\partial^2\mathfrak{P}_z}{\partial t^2} = \mathfrak{E}_z + \alpha\mathfrak{P}_z - f'\mathfrak{P}_z - g'\frac{\partial\mathfrak{P}_z}{\partial t}.$$

The equations may be further simplified, if, following a well known method, we work with complex expressions, all containing the time in the factor e^{int}. If we introduce the three quantities

$$\xi = f' - \alpha - m' n^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\eta = n g', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and

$$\zeta = \frac{n \mathbf{H}}{c N \mathbf{e}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

the result becomes

$$\left.\begin{aligned} \mathfrak{E}_x &= (\xi + i\eta)\,\mathfrak{P}_x - i\zeta\,\mathfrak{P}_y, \\ \mathfrak{E}_y &= (\xi + i\eta)\,\mathfrak{P}_y + i\zeta\,\mathfrak{P}_x, \\ \mathfrak{E}_z &= (\xi + i\eta)\,\mathfrak{P}_z. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

§ 5. Before proceeding further, we shall try to form an idea of the mechanism by which the absorption is produced. It seems difficult to admit the real existence of a resistance proportional to the velocity such as is represented by the expressions (8). It is true that in the theory of electrons a charged particle moving through the aether is acted on by a certain force to which the name of resistance may be applied, but this force is proportional to the differential coefficients of the third order of $\mathbf{x}, \mathbf{y}, \mathbf{z}$ with respect to the time. Besides, as we shall see later on, it is much too small to account for the absorption existing in many cases; we shall therefore begin by neglecting it altogether, i.e. by supposing that a vibrating electron is not subject to any force, exerted by the aether and tending to damp its vibrations.

However, if, in our case of gaseous bodies, we think of the mutual encounters between the molecules, a way in which the regular vibrations of light might be transformed into an inorderly motion that may be called heat, can easily be conceived. As long as a molecule is not struck by another, the movable electron contained within it may be considered as free to follow the periodic electric forces existing in the beam of light; it will therefore take a motion whose amplitude would continually increase if the frequency of the incident light corresponded exactly to that of the free vibrations of the electron.

In a short time however, the molecule will strike against another particle, and it seems natural to suppose that by this encounter the regular vibration set up in the molecule will be changed into a motion of a wholly different kind. Between this transformation and the next encounter, there will again be an interval of time during which a new regular vibration is given to the electron. It is clear that in this way, as well as by a resistance proportional to the velo-

city, the amplitude of the vibrations will be prevented from surpassing a certain limit.

We should be led into serious mathematical difficulties, if, in following up this idea, we were to consider the motions actually taking place in a system of molecules. In order to simplify the problem, without materially changing the circumstances of the case, we shall suppose each molecule to remain in its place, the state of vibration being disturbed over and over again by a large number of blows, distributed in the system according to the laws of chance. Let A be the number of blows that are given to N molecules per unit of time, Then

$$\frac{N}{A} = \tau$$

may be said to be the mean length of time during which the vibration in a molecule is left undisturbed. It may further be shown that, at a definite instant, there are

$$\frac{N}{\tau} e^{-\frac{\vartheta}{\tau}} d\vartheta$$

molecules for which the time that has elapsed since the last blow lies between ϑ and $\vartheta + d\vartheta$.

§ 6. We have now to compare the influence of the just mentioned blows with that of a resistance whose intensity is determined by the coefficient g. In order to do this, we shall consider a molecule acted on by an external electric force

$$a e^{int}$$

in the direction of the axis of x.

If there is a resistance g, the displacement $\mathbf{x}$ is given by the equation

$$m \frac{d^2\mathbf{x}}{dt^2} = -f\mathbf{x} - g \frac{d\mathbf{x}}{dt} + a\mathbf{e} e^{int},$$

so that, if we confine ourselves to the particular solution in which $\mathbf{x}$ contains the factor e^{int}, and if we use the relation (7),

$$\mathbf{x} = \frac{a\mathbf{e}}{m(n_0^2 - n^2) + ing} e^{int} \quad \ldots\ldots \quad (15)$$

In the other case, if, between two successive blows, there is no resistance, we must start from the equation of motion

$$m \frac{d^2\mathbf{x}}{dt^2} = -f\mathbf{x} + a\mathbf{e} e^{int},$$

whose general solution is

$$\mathbf{x} = \frac{a\,\mathbf{e}\,e^{int}}{m(n_0^2 - n^2)} + C_1 e^{i n_0 t} + C_2 e^{-i n_0 t} \quad . \quad . \quad . \quad . \quad (16)$$

By means of this formula we can calculate, for a definite instant t, the mean value $\bar{\mathbf{x}}$ for a large number of molecules, all acted on by the same electric force $a\,e^{i n t}$. Now, for each molecule, the constants C_1 and C_2 are determined by the values of $\mathbf{x}$ and $\frac{d\mathbf{x}}{dt}$ immediately after the last blow, i. e. by the values $\mathbf{x}_0$ and $\left(\frac{d\mathbf{x}}{dt}\right)_0$ existing at the time $t - \vartheta$, if ϑ is the interval that has elapsed since that blow. We shall suppose that immediately after a blow all directions of the displacement and the velocity of the electron are equally probable. Then the mean values of $\mathbf{x}_0$ and $\left(\frac{d\mathbf{x}}{dt}\right)_0$ are 0, and we shall find the exact value of $\bar{\mathbf{x}}$, if in the determination of C_1 and C_2, we suppose $\mathbf{x}$ and $\frac{d\mathbf{x}}{dt}$ to vanish at the time $t - \vartheta$.

In this way, (16) becomes

$$\mathbf{x} = \frac{a\,\mathbf{e}\,e^{int}}{m(n_0^2 - n^2)} \left\{ 1 - \frac{1}{2}\left(1 + \frac{n}{n_0}\right) e^{i(n_0 - n)\vartheta} - \frac{1}{2}\left(1 - \frac{n}{n_0}\right) e^{-i(n_0 + n)\vartheta} \right\}.$$

From this $\bar{\mathbf{x}}$ is found, if, after multiplying by $\frac{1}{\tau} e^{-\frac{\vartheta}{\tau}} d\vartheta$, we integrate from $\vartheta = 0$ to $\vartheta = \infty$. If u is an imaginary constant, we have

$$\frac{1}{\tau}\int_0^\infty e^{u\vartheta - \frac{\vartheta}{\tau}} d\vartheta = \frac{1}{1 - u\tau}.$$

Hence, after some transformations,

$$\bar{\mathbf{x}} = \frac{a\,\mathbf{e}}{m\left(n_0^2 + \frac{1}{\tau^2} - n^2\right) + 2\frac{imn}{\tau}} e^{i n t} \quad . \quad . \quad . \quad . \quad (17)$$

If this is compared with (15), it appears that, on account of the blows, the phenomena will be the same as if there were a resistance determined by

$$g = \frac{2\,m}{\tau} \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and an elastic force having for its coefficient

$$(f) = f + \frac{m}{\tau^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Indeed, if the elastic force had the intensity corresponding to this formula, the square of the frequency of the free vibrations would have, by (7), the value $n_0^2 + \frac{1}{\tau^2}$. The equation (15) would then take the form (17).

In the next paragraphs the last term in (19) will however be omitted.

As to the time τ, it will be found to be considerably shorter than the time between two successive encounters of a molecule. Hence, if we wish to maintain the conception here set forth, we must suppose the regular succession of vibrations to be disturbed by some unknown action much more rapidly than it would be by the encounters.

We may add that, even if there were a resistance proportional to the velocity, the vibrations might be said to go on undisturbed only for a limited length of time. On account of the damping their amplitude would be considerably diminished in a time of the order of magnitude $\frac{m}{g}$. This is comparable to the value of τ which, by (18), corresponds to a given magnitude of g.

§ 7. The laws of propagation of electric vibrations are easily deduced from our fundamental equations. We shall begin by supposing that there is no external magnetic field, so that the terms with ζ disappear from the equations (14).

Let the propagation take place in the direction of the axis of z and let the components of the electromagnetic vectors all contain the factor

$$e^{in(t-qz)}, \quad \ldots\ldots\ldots \quad (20)$$

in which it is the value of the constant q that will chiefly interest us. There can exist a state of things, in which the electric vibrations are parallel to OX and the magnetic ones parallel to OY, so that $\mathfrak{E}_x$, $\mathfrak{P}_x$, $\mathfrak{D}_x$ and $\mathfrak{H}_y$ are the only components differing from 0. Since differentiations with respect to t and to z are equivalent to a multiplication by in and by $-inq$ respectively, we have by (2) and (3)

$$q\,\mathfrak{H}_y = \frac{1}{c}\,\mathfrak{D}_x, \qquad q\,\mathfrak{E}_x = \frac{1}{c}\,\mathfrak{H}_y.$$

Hence

$$\mathfrak{D}_x = c^2 q^2\,\mathfrak{E}_x$$

and, in virtue of (1),

$$\mathfrak{P}_x = (c^2 q^2 - 1)\,\mathfrak{E}_x.$$

The first of the equations (14) leads therefore to the following

formula, which may serve for the determination of q,

$$c^2 q^2 - 1 = \frac{1}{\xi + i\eta} \quad \ldots\ldots\ldots \quad (21)$$

Of course, q has a complex value. If, taking $\varkappa$ and ω real, we put

$$q = \frac{1 - i\varkappa}{\omega}, \quad \ldots\ldots\ldots \quad (22)$$

the expression (20) becomes

$$e^{in\left(t - \frac{1 - i\varkappa}{\omega}\right)z},$$

so that the real parts of the quantities representing the vibrations contain the factor

$$e^{-\frac{n\varkappa}{\omega}z} \quad \ldots\ldots\ldots \quad (23)$$

multiplied by the cosine or sine of

$$n\left(t - \frac{z}{\omega}\right).$$

It appears from this that ω may be called the velocity of propagation and that the absorption is determined by $\varkappa$. If

$$\frac{n\varkappa}{\omega} = k,$$

(index of absorption), we may infer from (23) that, while the vibrations travel over a distance $\frac{1}{k}$, their amplitude is diminished in the ratio of 1 to $\frac{1}{e}$.

In order to determine ω and $\varkappa$, we have only to substitute (22) in (21). We then get

$$\frac{c^2(1 - i\varkappa)^2}{\omega^2} = 1 + \frac{1}{\xi + i\eta},$$

or, separating the real and the imaginary parts,

$$\frac{c^2(1 - \varkappa^2)}{\omega^2} = 1 + \frac{\xi}{\xi^2 + \eta^2}, \qquad \frac{2c^2\varkappa}{\omega^2} = \frac{\eta}{\xi^2 + \eta^2},$$

from which we derive the formulae

$$2\frac{c^2}{\omega^2} = \sqrt{\frac{(\xi + 1)^2 + \eta^2}{\xi^2 + \eta^2}} + \frac{\xi}{\xi^2 + \eta^2} + 1, \quad \ldots \quad (24)$$

$$2\frac{c^2\varkappa^2}{\omega^2} = \sqrt{\frac{(\xi + 1)^2 + \eta^2}{\xi^2 + \eta^2}} - \frac{\xi}{\xi^2 + \eta^2} - 1, \quad \ldots \quad (25)$$

in which the radical must be taken with the positive sign.

If the different constants are known, we can calculate by these formulae the velocity and the index of absorption for every value of the frequency n; in doing so, we shall also get an idea about the breadth and the intensity of the absorption band.

§ 8. In these questions much depends on the value of η. In the special case $\xi = 0$, i. e. if the frequency is equal to, or at least only a little different from that of the free vibrations, we have on account of (25)

$$2\frac{c^2\varkappa^2}{\omega^2} = \sqrt{1+\frac{1}{\eta^2}} - 1.$$

From what has been said above, it may further be inferred that along a distance equal to the wave-length in air, i. e. $\frac{2\pi c}{n}$, the amplitude decreases in the ratio of 1 to

$$e^{-\frac{2\pi c\varkappa}{\omega}}$$

Now, in the large majority of cases, the absorption along such a distance is undoubtedly very feeble, so that $\frac{2\pi c\varkappa}{\omega}$ must be a small number. The value of $\frac{c^2\varkappa^2}{\omega^2}$ must be still smaller and this can only be the case, if η is much larger than 1.

This being so, the radical in (25) may be replaced by an approximate value. Putting it in the form

$$\sqrt{1+\frac{2\xi+1}{\xi^2+\eta^2}},$$

we may in the first place observe, that, since η is large, the numerator $2\xi+1$ will be very small in comparison with the denominator, whatever be the value of ξ. Up to terms with the square of $\frac{2\xi+1}{\xi^2+\eta^2}$, we may therefore write for the radical

$$1+\frac{1}{2}\frac{2\xi+1}{\xi^2+\eta^2} - \frac{1}{8}\frac{(2\xi+1)^2}{(\xi^2+\eta^2)^2}$$

and after some transformations

$$2\frac{c^2\varkappa^2}{\omega^2} = \frac{4\eta^2-4\xi-1}{8(\xi^2+\eta^2)^2}.$$

As long as ξ is small in comparison with η^2, the numerator of this fraction may be replaced by $4\eta^2$. On the other hand, as

soon as ξ is of the same order of magnitude as η^2 or surpasses this quantity, the fraction becomes so small that it may be neglected, and it will remain so, if we omit the term -4ξ in the numerator. We may therefore write in all cases

$$\frac{c\varkappa}{\omega} = \frac{\eta}{2(\xi^2+\eta^2)},$$

so that the index of absorption becomes

$$k = \frac{n}{2c} \cdot \frac{\eta}{\xi^2+\eta^2} \quad \ldots\ldots\ldots \quad (26)$$

This formula shows that for $\xi = 0$ the index has its maximum value

$$k_0 = \frac{n}{2c\eta} \quad \ldots\ldots\ldots \quad (27)$$

and that for $\xi = \pm\, \nu\eta$, it is ν^2+1 times smaller.

The frequency corresponding to this value of ξ can easily be calculated. If a may be neglected, a question to which we shall return in § 18, (11) may be put in the form

$$\xi = m' (n_0^2 - n^2) \quad \ldots\ldots\ldots \quad (28)$$

Hence, for $\xi = \mp\, \nu\eta$

$$m' (n^2 - n_0^2) = \pm\, \nu\eta = \pm\, \nu\, n\, g',$$

or, on account of (10) and (18),

$$m (n^2 - n_0^2) = \pm\, \nu\, n\, g = \pm \frac{2\, m\, \nu\, n}{\tau},$$

$$n^2 - n_0^2 = \pm \frac{2\, \nu\, n}{\tau}.$$

If $n - n_0$ is much smaller than n_0, we may also write

$$n = n_0 \pm \frac{\nu}{\tau} \quad \ldots\ldots\ldots \quad (29)$$

The preceding considerations lead to the well known conclusion, somewhat paradoxal at first sight, that the intensity of the maximum absorption increases by a diminution of the resistance, or by a lengthening of the time during which the vibrations go on undisturbed. Indeed, if g is diminished or τ increased, it appears by (10) and (12) that η becomes smaller and by (27) k_0 will become larger. This result may be understood, if we keep in mind that, in the case $n = n_0$, the one most favourable to "optical resonance"; in molecules that are left to themselves for a long time a large amount of vibratory energy will have accumulated before a blow takes place. Though the blows are rare, the amount of vibratory energy which is converted into heat may therefore very well be large.

In another sense, however, the absorption may be said to be diminished by an increase of τ (or a diminution of g), the range of wave-lengths to which it is confined, becoming narrower. This follows immediately from the equation (26). Let a fixed value be given to ξ, so that we fix our attention on a point of the spectrum, situated at a definite distance from the place of maximum absorption, and let η be gradually diminished. As soon as it has come below ξ, further diminution will lead to smaller values of k, i. e. to a smaller breadth of the band.

If g is very small, or τ very large, we shall observe a very narrow line of great intensity.

§ 9. The observation of the bands or lines of absorption, combined with the knowledge that has been obtained by other means of some of the quantities occurring in our formulae, enables us to determine the time τ and the number N of molecules per unit volume.

I shall perform these calculations for two rather different cases, viz. for the absorption of dark rays of heat by carbonic dioxyd and for the absorption in a sodium flame.

As soon as we know the breadth of the absorption band, or, more exactly, at what distance from the middle of the band the absorption has diminished in a certain ratio, the value of τ may be deduced from (29); we have only to remember that in this formula, n is the frequency for which the index of absorption is $\nu^2 + 1$ times smaller than the maximum n_0.

ANGSTROM [1]) has found that in the absorption band of carbonic dioxyd, whose middle corresponds to the wave-length $\lambda = 2{,}60\,\mu$, the index of absorption has approximately diminished to $\frac{1}{2} k_0$ for $\lambda = 2{,}30\,\mu$. This diminution corresponding to $\nu = 1$, we have by (29)

$$\frac{1}{\tau} = n - n_0 ,$$

if n_0 and n are the frequencies for the wave-lengths $2{,}60\,\mu$ and $2{,}30\,\mu$.

In this way I find

$$\tau = 10^{-14} \text{ sec.}$$

In the case of the absorption lines produced in the spectrum by a sodium flame, we cannot say at what distance from the middle the absorption has sunk to $\frac{1}{2} k_0$. We must therefore deduce the value of τ from the estimated breadth of the line. Though the value of ν corresponding to the border cannot be exactly indicated, we shall

[1]) K. ÅNGSTRÖM, Beiträge zur Kenntniss der Absorption der Wärmestrahlen durch die verschiedenen Bestandteile der Atmosphäre, Ann. Phys. Chem. **39** (1890), p. 267 (see p. 280).

probably be not far wrong, if we suppose it to lie between 3 and 6; this would imply that at the border the index of absorption lies between $\frac{1}{10} k_0$ and $\frac{1}{37} k_0$. If therefore n relates to the border, the formula (29) shows that the limits for $\frac{1}{\tau}$ are $\frac{1}{3}(n-n_0)$ and $\frac{1}{6}(n-n_0)$.

In HALLO's experiments the breadth of the D-lines was about 1 $A.E.$ The relation between n and the wave-length λ being

$$n = \frac{2\pi c}{\lambda},$$

we find for that between small variations of the two quantities

$$dn = -\frac{2\pi c}{\lambda^2} d\lambda.$$

Hence, if we put $d\lambda = 0{,}5\ A.E. = 0{,}5 \times 10^{-8}$ cm., we find

$$n - n_0 = 0{,}26 \times 10^{12},$$

from which I infer that the value of τ lies between 12×10^{-12} and 24×10^{-12} sec.

§ 10. In the case of carbonic dioxyd the number N may be deduced from the measured intensity of absorption. In ÅNGSTRÖM's experiments this amounted to 10,6 pCt. in a layer, 12 cm. thick, and for $\lambda = 2{,}60\,\mu$. The amplitude being diminished in the proportion of 1 to $e^{-k_0 z}$ in a layer whose thickness is z, and the intensity of the rays being proportional to the square of the amplitude, we have

$$e^{-24k_0} = 0{,}894,$$

and

$$k_0 = 0{,}0046.$$

Now, by the formulae (27), (12), (10) and (18)

$$k_0 = \frac{N\mathfrak{e}^2\tau}{4cm},$$

$$N = \frac{4cmk_0}{\mathfrak{e}^2\tau}.$$

Here τ and k_0 are known by what precedes. As to the charge $\mathfrak{e}$, it is, in all probability, equal to that of an electrolytic ion of hydrogen. It is therefore expressed in the usual electromagnetic units by the number $1{,}3 \times 10^{-20}$, and in the usual electrostatic units by $3{,}9 \times 10^{-10}$. The unit of electricity used in our formulae being $\sqrt{4\pi} = 3{,}5$ times smaller than the common electrostatic one, we must put

$$\mathfrak{e} = 14 \times 10^{-10}. \quad \ldots \quad (30)$$

In the case of the infra-red rays whose absorption has been measured by ÅNGSTRÖM we are probably concerned with the vibrations of charged atoms of oxygen or carbon. The mass of an atom of hydrogen being about $1{,}3 \times 10^{-24}$ gramme, I shall take

$$m = 2 \times 10^{-23}.$$

The result then becomes

$$N = 6 \times 10^{17}.$$

§ 11. The above method is not available for a sodium flame. HALLO has however observed that the value of N for this body may be deduced from his measurements of the magnetic rotation of the plane of polarization and GEEST has shown that the magnetic double refraction in the flame may serve for the same purpose. In what follows I shall only use one of HALLO's results.

In the first place it must be noticed that in the case to be considered, ξ is much larger and $\frac{\xi}{\xi^2+\eta^2}$ much smaller than unity. The radical in (24) may therefore be replaced by

$$1 + \frac{\xi}{\xi^2+\eta^2}$$

and the formula becomes

$$\frac{c}{\omega} = 1 + \frac{\xi}{2(\xi^2+\eta^2)}.$$

Now, if there is an external magnetic field, the velocities of propagation ω_1 and ω_2 of right and left circularly polarized light can be calculated by a similar formula. We have only to replace ξ by $\xi - \zeta$ and by $\xi + \zeta$.[1]) From the results

$$\frac{c}{\omega_1} = 1 + \frac{\xi-\zeta}{2[(\xi-\zeta)^2+\eta^2]} \text{ and } \frac{c}{\omega_2} = 1 + \frac{\xi+\zeta}{2[(\xi+\zeta)^2+\eta^2]}$$

we find for the angle of rotation per unit length

$$\varphi = \frac{1}{2} n \left(\frac{1}{\omega_1} - \frac{1}{\omega_2}\right) = \frac{n}{4c}\left\{\frac{\xi-\zeta}{(\xi-\zeta)^2+\eta^2} - \frac{\xi+\zeta}{(\xi+\zeta)^2+\eta^2}\right\} \quad . \quad . \quad . \quad (31)$$

In order to determine N by means of a measured value of φ, we begin by observing that, in virtue of the equation (28), for which we may write

$$\xi = 2m' n_0 (n_0 - n),$$

each value of ξ determines a certain point in the spectrum whose distance from the middle of the band is proportional to ξ. At the

[1]) See LORENTZ, Sur la théorie des phenomènes magnéto-optiques, etc., § 16.

border of the band (if there is no magnetic field) ξ has the value $v\eta$, the coefficient v being some moderate number, say between 3 and 6 (§ 9), and for one of the components of ZEEMAN's doublet we have $\xi = \zeta$. In the magnetic field used by HALLO the distance of the components from the middle of the original line amounted to 0,15 *A. E.*, half the breadth of the line being 0,5 *A. E.*, as has already been said.

We have therefore the following relation between η and ζ:

$$\zeta : v\eta = 0{,}15 : 0{,}5$$

$$\eta = \frac{3{,}3}{v}\zeta. \quad \ldots\ldots\ldots \quad (32)$$

On the other hand, a point in the spectrum, at which the angle of rotation per unit length was approximately equal to unity, was situated at a distance of 1,6 *A. E.* $\left(\frac{35}{130}\right.$ of the mutual distance of the two D-lines) from the middle of the original line. This being 10 times the distance from this line to one of the components, we have approximately

$$\xi = 10\,\zeta.$$

On substituting this value and (32) in the formula (31), it appears that the terms η^2 may be omitted. Hence, if (13) is taken into account,

$$\varphi = 0{,}005\frac{n}{c\zeta} = 0{,}005\frac{N\mathbf{e}}{\mathbf{H}}, \quad \ldots\ldots \quad (33)$$

or since $\varphi = 1$ is,

$$N\mathbf{e} = 200\,\mathbf{H}.$$

The strength of the magnetic field in these experiments was 9000 in ordinary units, or

$$\mathbf{H} = \frac{9000}{\sqrt{4\pi}} = 2600$$

in those used in our equations. Taking for $\mathbf{e}$ the value (30), I finally find

$$N = 4 \times 10^{14}.$$

§ 12. The value of η may likewise be calculated, both for the carbonic dioxyde and for the sodium flame. In the first case we can avail ourselves of the formula (27), in which k_0 is now known; the result is

$$\eta = \frac{n}{2ck_0} = \frac{\pi}{\lambda k_0} = 2{,}5 \times 10^6.$$

For the sodium flame we first draw from (33)

$$\zeta = 0{,}005\,\frac{n}{c} = 0{,}01\,\frac{\pi}{\lambda} = 500$$

and we then find by (32) the following limits for η

550 and 270.

These results fully verify our assumption that η would be a large number.

Finally we can compare the values we have found for τ with the period of the vibrations. In this way we see that in the flame some six or twelve thousand vibrations follow each other in uninterrupted succession. In the carbonic dioxyd on the contrary no more than a few vibrations can take place between two successive blows.

§ 13. After having found the number N of molecules in the sodium flame we can deduce from it the density d of the vapour of sodium. In doing so, I shall suppose the molecules to be single atoms, so that each has a mass equal to 23 times that of a mass of hydrogen. Taking for this latter $1{,}3 \times 10^{-24}$ gramme, I find

$$d = 12 \times 10^{-9}.$$

This is not very different from the number 7×10^{-9} found by HALLO.

HALLO has already pointed out that this value is very much smaller than the density of the vapour really present in the flame; at least, this must be concluded if we may apply a statement made by E. WIEDEMANN, according to which a certain flame with which he has worked contained per cm³. about 5×10^{-7} gramme of sodium. Perhaps the difference must be explained by supposing that only those particles that are in some peculiar state, a small portion of the whole number, play a part in the phenomenon of absorption. This would agree with the views to which LENARD has been led by his investigation of the emission by vapour of sodium.

It must be noticed that the value of N we have calculated for carbonic dioxyd warrants a similar conclusion. In the experiments of ÅNGSTRÖM the pressure was 739 mm. At this pressure and at 15° C. the number of molecules per cm³. may be estimated at $3{,}2 \times 10^{19}$. This is 50 times the number we have found in § 10.

§ 14. An interesting result is obtained if the time τ we have calculated for carbonic dioxyd is compared with the mean lapse of time between two successive encounters of a molecule. Under the circumstances mentioned at the end of § 13, the mean length of the free path is about 7×10^{-6} cm. The molecular velocity being 4×10^{4} cm. per sec., this distance is travelled over in

$$1{,}8 \times 10^{-10} \text{ sec.},$$

i. e. in a time equal to 18000 times the value we have found for τ. We see in this way that it cannot be the encounters between molecules, by which the regular succession of vibrations comes to an end. It seems to be disturbed much more rapidly by some other cause which is at work within each molecule.

In the case of the sodium flame there is a similar difference between the length of time τ and the mean interval between two encounters.

§ 15. We shall now return for a moment to the resistance that has been spoken of in § 5, the only one that is really exerted by the aether. This resistance is intimately connected with the radiation issuing from a vibrating electron, and if a beam of light were weakened by its influence, this would be due to part of the incident energy being withdrawn from the beam and emitted again into the aether. Of course, this could hardly be called an absorption. But, apart from this objection, we can easily show that the resistance in question is much too small to account for the diminution of intensity that is really observed. Its component in the direction of x is

$$\frac{\mathbf{e}^2}{6\pi c^3}\frac{d^3\mathbf{x}}{dt^3},$$

or, for harmonic vibrations of frequency n,

$$-\frac{n^2\mathbf{e}^2}{6\pi c^3}\frac{d\mathbf{x}}{dt}.$$

Comparing this with (8), we find

$$g = \frac{n^2\mathbf{e}^2}{6\pi c^3}.$$

This amounts to $2{,}0 \times 10^{-21}$ for carbonic dioxyd (for the wavelength $\lambda = 2{,}60\,\mu$ (§ 9)) and to $4{,}0 \times 10^{-20}$ in the case of the sodium flame. These numbers are far below those which result from (18), if we substitute the value that has been calculated for τ. We then get, for carbonic dioxyd $4{,}0 \times 10^{-9}$, and for the sodium flame a number between $1{,}2 \times 10^{-16}$ and $0{,}6 \times 10^{-16}$.

§ 16. It has already been shown in § 8 that an increase of η broadens the absorption band, diminishing at the same time the absorption in its middle. Indeed, in many cases we may say that the broader the band, the feebler is the absorption for a definite kind of rays.

The question now arises what is the total amount of energy

absorbed by a layer of given thickness z, if the incident beam contains all wave-lengths occurring in the part of the spectrum occupied by the absorption band. In treating this problem, I shall suppose the energy to be uniformly distributed over this range of frequencies, so that, if we write Idn for the incident energy, in so far as it belongs to wave-lengths between n and $n + dn$, I is a constant.

The total amount of energy absorbed is then given by

$$A = I\int_0^\infty (1 - e^{-2kz})\, dn \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Now, if the coefficient g and the time τ were independent of the density of the gas, both ξ and η would be inversely proportional to N; this results from (10), (12) and (28). The equation (26) shows that under these circumstances and for a given value of n, k is proportional to N. The value of A will therefore be determined by the product Nz. This means that the total absorption would solely depend on the quantity of gas contained in a layer of the given thickness, whose boundary surfaces have unit of area; if the same quantity were compressed within a layer of a thickness $\frac{1}{2}z$, the absorption would not be altered.

The result is different, if g and τ depend on the density. In order to examine this point, I shall take z to be so small that $1 - e^{-2kz}$ may be replaced by $2kz - 2k^2z^2$, so that (34) becomes

$$A = 2I\left\{z\int_0^\infty k dn - z^2\int_0^\infty k^2 dn\right\} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Let us further confine ourselves to an absorption band, so narrow, that we may put

$$\xi = 2m'n_0\,(n_0 - n), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$\eta = n_0 g', \; k = \frac{n_0}{2c}\frac{\eta}{\xi^2 + \eta^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Introducing ξ, instead of n, and extending the integrations from $\xi = -\infty$ to $\xi = +\infty$, as may indeed be done, I find from (35)

$$A = \frac{\pi I}{2cm'}\left(z - \frac{1}{4cg'}z^2\right),$$

or, on account of (10),

$$A = \frac{\pi I}{2cm}\left\{Ne^2 z - \frac{1}{4cg}(Ne^2 z)^2\right\}.$$

Two conclusions follow from this result. First, the absorption in an infinitely thin layer of given thickness does not depend on the

value of g. In the second place, if the layer is so thick that the second term in the formula has a certain influence, for a given value of Nz, the amount of absorption will increase with g. It will therefore increase by a compression of the gas, if by this means the coefficient g takes a larger value. An effect of this kind has really been observed by ÅNGSTRÖM [1]) in his experiments on the absorption produced by carbonic dioxyde.

This result could have been predicted by theory if the idea that the succession of regular vibrations would be disturbed by the collisions between the molecules had been confirmed; then, by an increase of the density, the time τ would become shorter and the formula (18) would give a larger value for the coefficient g. As it is, the vibrations must be supposed to be disturbed by some other cause (§ 14) and we can only infer from ÅNGSTRÖM's measurements that the influence of this cause must depend in some unknown way on the density of the gas.

§ 17. Thus far, we have constantly assumed in our calculations that the coefficient η is very much larger than unity; this hypothesis has been confirmed by the values given in § 12 and, to judge from these numbers, it would even seem hardly probable that η can in any case have a value equal to, or smaller than 1. Yet, there is a phenomenon which can only be explained by ascribing to η a small value. This is the dissymmetry of the ZEEMAN effect, which has been predicted by VOIGT's theory [2]) and has shown itself in some experiments of ZEEMAN [3]). In so far as we are here concerned with it, it consists in a small inequality, observable only in weak magnetic fields, of the distances at which the two outer components of the triplet are situated from the place of the original spectral line. Whereas in strong fields the position of these components is determined by the equations $\xi = +\zeta$ and $\xi = -\zeta$, it corresponds to $\xi = 0$ and $\xi = 1$, if the magnetic intensity is very small.

VOIGT has immediately pointed out that the dissymmetry can only exist, if η is not very large. Yet, from the fact that the effect could scarcely be detected by ZEEMAN, he concludes that the coefficient must

[1]) ÅNGSTRÖM, Über die Abhängigkeit der Absorption der Gase, besonders der Kohlensäure, von der Dichte, Ann. Phys., 6 (1901), p. 163.

[2]) VOIGT, Über eine Dissymmetrie der ZEEMAN'schen normalen Triplets, Ann. Phys., 1 (1900), p. 376.

[3]) ZEEMAN, Some observations concerning an asymmetrical change of the spectral lines of iron, radiating in a magnetic field. These Proceedings, II (1900), p. 298.

have been rather larger than unity. In my opinion, we must go farther than that and ascribe to η a value, not sensibly above 1, my argument being that the dissymmetry can only make itself felt, if the difference between the distances from the original line to the two components in question is not very much smaller than the breadth of the line.

We know already (§ 9) that $\xi = 0$ at the middle of the line and $\xi = v\eta$ at the border. Now, if η were sensibly larger than 1, the places corresponding to $\xi = 0$ and $\xi = 1$, i. e. the places occupied by the two components in a weak field, would lie within the breadth of the original line; it would therefore be impossible to discern the want of symmetry.

§ 18. Whatever be the exact value of η, ZEEMAN's experiments on this point show at all events that under favourable circumstances a displacement of a line, corresponding to a change from $\xi = 0$ to $\xi = 1$, or to a change

$$\frac{1}{2m'n_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

of the frequency, is large enough to be seen. But, if such is the case, we shall no longer be right, if we discuss the value of ξ, in omitting quantities that are but a few times smaller than unity.

A quantity of this kind is the term α in the equation (11), which as has already been mentioned, is but little different from $^1/_3$, and which we have omitted in all our calculations. If we wish to take it into account, we shall find that all that precedes will still hold, provided only we replace n_0 by the quantity n'_0, determined by

$$f' - \alpha = m' n'^2_0 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Indeed, (28) may then be written in the form

$$\xi = m' (n'^2_0 - n^2) ,$$

and the place of maximum absorption, the middle of the line, will correspond to the frequency n_0, exactly as it formerly corresponded to the frequency n'_0.

Now, by (7) and (10)

$$f' = m' n_0^2 ,$$

and by (39)

$$n'^2_0 = n_0^2 - \frac{\alpha}{m'} \, , \quad n'_0 = n_0 - \frac{\alpha}{2n_0 m'} \quad . \quad . \quad . \quad . \quad (40)$$

or, on account of (10),

$$n'_0 = n_0 - \frac{\alpha N e^2}{2 n_0 m} \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

We learn from this equation that an increase of the density must

give rise to a small displacement of the absorption line towards the side of the larger wave-lengths. A shift of this kind has been observed by HUMPHREYS and MOHLER in their investigation of the influence of pressure on the position of spectral lines. However, as the formula (41) does not lead to the laws the two physicists have established for the new phenomenon, I do not pretend to have given an explanation of it.

Nevertheless we may be sure that in those cases in which the dissymmetry of the ZEEMAN effect can be detected, the last term in (41), which in fact is of the same order of magnitude as the expression (38), can have an influence on the position of a spectral line that is not wholly to be neglected.

On the other hand, it now becomes clear that, in the case of a large value of η, the term α in (11) may certainly be neglected, its influence on the position of the middle of the line being much smaller than the breadth. [1])

§ 19. We shall conclude by examining the influence of the last term in (19), which we have likewise omitted. If we replace f by $f + \frac{m}{\tau^2}$ and, in virtue of (10), f' by $f' + \frac{m'}{\tau^2}$, which I shall denote by (f'), and if this time we neglect the term α, the formula (11) may again be written in the form (28). Indeed, if we put

$$n''_0{}^2 = \frac{(f')}{m'} = n_0{}^2 + \frac{1}{\tau^2}, \quad \ldots\ldots\ldots \quad (42)$$

we shall have

$$\xi = m' (n''_0{}^2 - n^2).$$

Instead of (42) we may write

$$n''_0 = n_0 + \frac{1}{2 n_0 \tau^2}, \quad \ldots\ldots\ldots \quad (43)$$

an equation which shows that the absorption band lies somewhat more towards the side of the smaller wave-lengths than would correspond to the frequency n_0 and that its position would be shifted a little, if the time τ were altered in one way or another (§ 16). These displa-

[1]) Prof. JULIUS has called my attention to the fact that in many cases the absorption lines are considerably broadened by the change in the course of the rays that can be produced in a non-homogeneous medium by anomalous dispersion. In the experiments of HALLO, I have discussed, this phenomenon seems to have had no influence. This may be inferred from the circumstance that the emission lines of his flame had about the same breadth as the absorption lines.

cements would however be much smaller than half the breadth of the band. This is easily seen, if we divide the value of $n''_0 - n_0$ calculated from (43) by the value of $n - n_0$ that is given by (29). The result

$$\frac{1}{2\,\nu\,n_0\,\tau}$$

is (cf. § 12) a small fraction, because $n_0\,\tau$ is equal to the number of vibrations during the time τ, multiplied by $2\,\pi$.

(January 25, 1906).