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Physics. — *"The width of spectral lines."* By Prof. H. A. LORENTZ.

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§ 1   In order to account for the absorption of light we may suppose the molecules to contain electrons which are set vibrating by the incident rays and experience a resistance to their motion.

If we suppose that an electron is drawn towards its position of equilibrium by a quasi-elastic force and that the resistance is proportional to the velocity, the vibrations are determined by the equation

$$m\ddot{\mathbf{r}} = -f\mathbf{r} - g\dot{\mathbf{r}} + e\mathbf{E}, \quad \ldots \ldots \quad (1)$$

where the vector $\mathbf{r}$ means the displacement from the position of equilibrium and $\mathbf{E}$ the electric force in the incident light. The mass and the charge are represented by m and e, whereas f and g are the constants for the quasi-elastic force and the resistance.

The theory takes its simplest form for a gaseous body of not too great a density, to this case I shall here confine myself. If there are several groups of electrons, those which belong to the same group being equal and equally displaced, we may write for the electric moment per unit of volume

$$\mathbf{P} = \Sigma N e\mathbf{r}, \quad \ldots \ldots \ldots \quad (2)$$

where the sign Σ refers to the different groups and N means the number of electrons per unit of volume for each group. The dielectric displacement is given by

$$\mathbf{D} = \mathbf{E} + \mathbf{P}$$

and in addition to these formulae we have the general equations

$$\mathrm{rot\ H} = \frac{1}{c}\,\dot{\mathrm{D}},$$

$$\mathrm{rot\ E} = -\frac{1}{c}\,\dot{\mathrm{H}}.$$

(H magnetic force, c velocity of light in the aether).

We shall, in the usual way, represent the vibrations of the system by means of complex expressions, so that, if n is the frequency, all variable quantities contain the factor

$$e^{int}.$$

Introducing

$$n_0 = \sqrt{\frac{f}{m}},$$

the frequency of the free vibrations, we find from (1) and (2)

$$\mathrm{P} = \Sigma\,\frac{N e^2}{m(n_0{}^2 - n^2) + ing}\,\mathrm{E}.$$

A beam of light travelling in the direction of the axis of x, may be represented by expressions for E, D and H, containing the factor

$$e^{in\left(t - \frac{(\mu)x}{c}\right)},$$

where (μ) may be called the 'complex index of refraction." For this quantity we find from the above equations

$$(\mu)^2 = 1 + \Sigma\,\frac{N e^2}{m(n_0{}^2 - n^2) + ing}\quad\cdots\cdots\quad(3)$$

§. 2. If now we put

$$(\mu) = \mu - \frac{ich}{n}, \quad\cdots\cdots\cdots\quad(4)$$

μ will be the real index of refraction and h the index of absorption. The meaning of the latter is, that the intensity of a beam of light travelling over a distance d, is diminished in the ratio of 1 to

$$e^{-2hd}\quad\cdots\cdots\cdots\cdots\quad(5)$$

By means of (3) μ and h may be determined for each frequency of the light.

If the values of n_0 for the different groups of electrons are sufficiently different from each other, there will be a certain number of separate maxima of absorption. In this case we may treat the phenomena belonging to each of these maxima with sufficient approximation by supposing only one group of corpuscles to be present.

Thus (3) becomes

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$$(\mu)^2 = 1 + \frac{Ne^2}{m(n_0^2 - n^2) + ing} , \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

and if we put

$$\frac{Ne^2}{n_0 g} = \alpha, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

we find the following values for the case $n = n_0$, i.e. for the maximum of absorption

$$(\mu_0)^2 = 1 - i\alpha,$$

$$2\mu_0^2 = \sqrt{1 + \alpha^2} + 1,$$

$$2\frac{c^2 h_0^2}{n_0^2} = \sqrt{1 + \alpha^2} - 1.$$

The last equation shows that the smaller the coefficient of resistance g, the greater will be the value of h_0; small resistances give rise to a strong maximum of absorption. We can in this respect distinguish two extreme cases; viz. that α is much greater and that it is considerably smaller than unity. In the first case we have approximately

$$\frac{ch_0}{n_0} = \sqrt{\tfrac{1}{2}\alpha}$$

and in the second case

$$\frac{ch_0}{n_0} = \tfrac{1}{2}\alpha \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

If we write λ_0 for the wave-length in the aether, corresponding to n_0, we have

$$\frac{ch_0}{n_0} = \frac{h_0 \lambda_0}{2\pi}.$$

Now, according to (5) the decrease in intensity over a wave-length's distance is given by

$$e^{-2h_0 \lambda_0} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

and we see therefore that this decrease will be considerable if $\alpha \gg 1$ and very small if $\alpha \ll 1$.

§ 3. The width of the bands of absorption may likewise be deduced from equation (6). Indeed, if n is made to differ from n_0 in one direction or the other, the term $m(n_0^2 - n^2)$ gains in importance in comparison with ing; when it has reached a value equal to a few times ng, the index of absorption has become considerably smaller than h_0. As the ratio of $m(n_0^2 - n^2)$ to ng is of the same order of magnitude as that of $2mn_0(n - n_0)$ to $n_0 g$, we may say that for

$$n - n_0 = \pm s \cdot \frac{g}{2m}, \quad \cdots \cdots \quad (10)$$

where s is a moderate number, the absorption is much smaller than for $n - n_0$. Hence, the absolute value of (10) will give us some idea of half the width of the absorption band. The smaller the coefficient of resistance, the narrower the band is seen to be. A strong maximum of absorption and a small width will be found together, whereas in the case of a feeble maximum we shall find a broad band.

For values of n, differing so much from n_0 that $i\,n\,g$ may be treated as a small quantity compared with $m(n_0{}^2 - n^2)$, we may replace (6) by

$$(\mu)^2 = 1 + \frac{Ne^2}{m(n_0{}^2 - n^2)} - \frac{iNn\,e^2 g}{m^2(n_0{}^2 - n^2)^2}.$$

Supposing further that the real part on the right hand side is positive and much greater than the imaginary one, we find approximately

$$\mu^2 = 1 + \frac{Ne^2}{m(n_0{}^2 - n^2)},$$

$$h = \frac{Ne^2 n^2}{2\mu c m^2 (n_0{}^2 - n^2)^2} g.$$

The last formula shows that the absorption at a rather large distance from the maximum increases with the coefficient of resistance, just the reverse of what we found for the maximum itself.

For values of g, so great that $\alpha \ll 1$, the equations become less complicated. Indeed, for this case (6) may be written

$$(\mu) = 1 + \frac{1}{2} \cdot \frac{Ne^2}{m(n_0{}^2 - n^2) + i n g}$$

and this, combined with (4), leads to the values

$$\mu = 1 + \frac{1}{2} \cdot \frac{Ne^2 m(n_0{}^2 - n^2)}{m^2(n^2 - n_0{}^2)^2 + n^2 g^2},$$

$$h = \frac{1}{2c} \cdot \frac{Ne^2 n^2 g}{m^2(n^2 - n_0{}^2)^2 + n^2 g^2}.$$

This last equation shows that for $n = n_0$

$$h_0 = \frac{Ne^2}{2cg},$$

agreeing with (8), and that at the distance from the maximum determined by (10), the index of absorption has become $s^2 + 1$ times smaller than h_0.

§ 4. The above has been known for a long time and has been repeated here as an introduction only to some further considerations. These will be limited to lines in the visible and the ultraviolet spectrum, i.e. to lines which in all probability are due to vibrations of *negative* electrons.

We shall also confine ourselves to such problems as may be treated without going deeply into the mechanism of the absorption. There are good grounds for this restriction, for it must be owned that in many cases we are very uncertain about the true nature of the phenomenon.

In the case of a vibrating electron there is always a resistance of *one* kind, viz. the force that is represented by

$$\frac{e^2}{6\pi c^3}\ddot{v},$$

if v is the velocity. For harmonic vibrations we may write for it

$$-\frac{e^2 n^2}{6\pi c^3}v,$$

so that it proves to be proportional to the velocity and opposite to it. If this "radiation resistance", as it may appropriately be called, because it is intimately connected with the radiation issuing from the particle, is the only one, we must substitute in the above formulae for the coefficient g the value

$$g_1 = \frac{e^2 n^2}{6\pi c^3} \quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad (11)$$

Replacing here n by n_0 we deduce from form. (7)

$$\alpha = \frac{6\pi N c^3}{n_0^3} = \frac{3}{4\pi^2} N\lambda_0^3.$$

Now $N\lambda_0^3$, the number of vibrating electrons in a "cubic wavelength" will have in many cases a high value. Hence, on our present assumption, α would be very great and for rays of frequency n_0 the weakening would be considerable even over a distance of one wave-length only. Indeed, one finds for the exponent in (9)

$$2h_0\lambda_0 = -\sqrt{6N\lambda_0^3} \quad\cdot\quad\quad\cdot\quad\quad\cdot\quad\quad\cdot\quad (12)$$

It must be remarked here that in the case now under consideration, we cannot speak of true "absorption", i.e. of transformation of the vibrations into irregular heat motion, but only of a "scattering" or the light by the vibrating electrons, so that it may properly be called the "index of extinction".

Formula (11) leads to a very small value for the width of the dark line. Indeed using (10) and replacing by n (11) we easily find for the width measured by the difference of wave-length

between the borders

$$\Delta\lambda = s\,\frac{g_1}{mn_0}\,\lambda_0 = s\,\frac{e^2 n_0 \lambda_0}{6\pi c^3 m},$$

or

$$-\,\Delta\lambda = 2\pi\,sR,$$

after substitution of the well known value

$$m = \frac{e^2}{6\pi c^2 R}$$

(R radius of the electron) for the (electromagnetic) mass m.

Now we have

$$R = 1{,}25\,.\,10^{-13}\,\text{cm},$$

so that for $s = 10$

$$\Delta\lambda = 12.10^{-12}\,\text{cm} = 0{,}0012\,\overset{\circ}{\text{A}}\,\text{U.,}\quad\ldots\ldots \quad (13)$$

This is a very small width indeed.

We shall soon see however that equations (12) and (13) apply to the ideal case only of molecules having no velocity of translation. In reality, on account of the heat motion of the molecules a "line of extinction" will be much broader than is given by (13) and less strong at the middle than we should infer from (12).

One remark more has to be made about the radiation resistance. Though the extinction to which it gives rise, quickly decreases as the frequency n deviates more and more from the frequency n_0, yet in the case of thick layers of gas it remains observable at a considerable distance from n_0. We may suppose e.g. that in the case of atmospheric air, n_0 belongs to a point in the ultraviolet. Now, if for light in the visible spectrum, we calculate the extinction corresponding to the coefficient g_1, we find exactly the well known formula of RAYLEIGH which agrees in a satisfactory way with observations.

§ 5. As the radiation resistance does not give rise to any true absorption, we must look for another explanation of this phenomenon. We can hardly think of a real friction or viscosity, but we may suppose that the vibrations of the electrons which are excited by the incident light cannot go on regularly for a long time, but are disturbed over and over again by collisions or impacts which convert them into irregular heat motion. It can be shown[1] that this leads to the same effect as a frictional resistance and that the

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[1] H. A. Lorentz, The absorption and emission lines of gaseous bodies, Proc. Amsterdam Acad. 8 (1905), p. 591.

formulae of §§ 1 and 2 may still be used, provided we substitute for the coefficient g the value

$$g_2 = \frac{2m}{\tau}. \qquad \qquad (14)$$

Here τ denotes the average time between two succeeding collisions of one and the same electron. The formula is based on the assumption that each collision wholly destroys the original vibration. If some part of it remained after an impact, we should have to take for τ a larger or smaller multiple of the time between two collisions. We may also remark that the expression (14) has a more general meaning. We may understand by τ the time during which a vibration can go on without being much disturbed or considerably damped, and use the formula, whatever be the cause of the disturbance or the damping. If there were e.g. a true frictional resistance the equation for the free vibrations would be

$$m\,\ddot{r} = -f\,r - g\,\dot{r},$$

and we should have

$$r = a\,e^{-\frac{g}{2m}t} \cos \sqrt{\frac{f}{m} - \frac{g^2}{4m^2}}\,t.$$

The time during which the amplitude decreases in the ratio $e : 1$ would therefore be

$$\tau = \frac{2m}{g},$$

which agrees with (14). Thus, the formula also applies to cases in which there is a radiation resistance only; for g we have then to substitute the value (11).

Returning to the question of impacts, we may remark that in the case of a gaseous medium, it would be natural to take for τ in (14) the mean time between two collisions of a molecule. There are, however, cases where we find in this way a value much too high for g_2.

Let us consider e.g. the propagation of yellow light $(\lambda = 6000\,\text{Å. U.})$ through air of 0° and under a pressure of 76 cm, and compare the values of g_1 and g_2. In calculating this latter coefficient we shall use the values holding for nitrogen. If u denotes the mean velocity of the molecules, l the mean length of path between two collisions, we find, putting $\tau = \dfrac{l}{u}$, from (14) and (11)

$$\frac{g_2}{g_1} = \frac{1}{2\pi^2}\,\frac{u}{c}\cdot\frac{\lambda^2}{Rl}.$$

With $\lambda = 6.10^{-5}$ cm, $l = 9,4.10^{-6}$ cm, $u = 4,93.10^{4}$ cm/sec , and the above value of R, the ratio becomes

$$\frac{g_2}{g_1} = 172.$$

Now, we found in § 3 that, at a rather large distance from n_0, the index of absorption is proportional to g. Our calculation therefore shows that the collisions would cause an extinction 172 times stronger than that to which the radiation resistance gives rise. As the latter leads to RAYLEIGH's formula which has been confirmed by the observations, we must conclude that the effect of the collisions is much less than we supposed it to be. Thus, when light is propagated in air the electric moment which is excited in a molecule must remain nearly unchanged in direction and magnitude during an impact.

Of course, notwithstanding this, it may very well be that in the neighbourhood of n_0 and under special circumstances the collisions disturb the vibrations. Recently STARK has given good reasons for supposing that the electric field round a charged particle changes the vibrations of a neighbouring molecule in such a way that a broadening of the spectral line is brought about.

§ 6. It has often been remarked that, according to DOPPLER's principle, the molecular motion must give rise to a broadening of the spectral lines. We shall first consider this effect for the case of an emission line, on the assumption that there are no other causes for a broadening.

Let n_0, the frequency of the vibrations within the molecules, be the same for all the particles and let ξ denote the component of the velocity of a molecule along a line directed towards the observer, ξ being positive when the molecule approaches the observer, and negative in the opposite case. Then the observed frequency is given by

$$n = n_0 \left(1 + \frac{\xi}{c} \right).$$

The change in frequency expressed in terms of n_0, i.e. the fraction

$$\omega = \frac{n - n_0}{n_0},$$

which also represents the ratio of the change of wave-length to λ_0, is therefore given by

$$\omega = \frac{\xi}{c} \qquad \ldots \ldots \ldots \ldots \quad (15)$$

Let us further write N for the number of molecules per unit of volume and u^2 for the mean square of their velocity. Then we find

for the number of particles for which the velocity ξ lies between ξ and $\xi + d\xi$, and the change of frequency between the corresponding values ω and $\omega + d\omega$,

$$\sqrt{\frac{3}{2\pi}} \frac{N}{u} e^{-\frac{3\xi^2}{2u^2}} d\xi \quad \ldots \ldots \ldots \ldots (16)$$

or

$$\sqrt{\frac{3}{2\pi}} \frac{c}{u} Ne^{-\frac{3c^2}{2u^2}\omega^2} d\omega \quad \ldots \ldots \ldots (17)$$

This last expression immediately determines the distribution of light in the emission line. The borders of the line may be taken to correspond to the values of ω for which the exponent becomes -1, i. e. to

$$\omega = \sqrt{\frac{2}{3}} \frac{u}{c},$$

so that the width is determined by

$$\Delta\lambda = 2 \sqrt{\frac{2}{3}} \frac{u}{c} \cdot \lambda_0.$$

If u is of the order of 5.10^4 cm/sec and λ_0 of the order of 6000 Å.U., this $\Delta\lambda$ will be about $1/60$ Å.U. This is a very small width; yet, it far exceeds the value which, starting from the value of g_1, we found (§ 4) for the breadth of an absorption line, and which would also belong to an emission line, if we had to reckon with the radiation resistance only. The cause of the difference is that

$$g_1 \ll m n_0 \frac{u}{c} \quad \ldots \ldots \ldots \ldots (18)$$

The conclusions drawn from (17) about the width of the lines are in good agreement with the results of several physicists; they are strikingly confirmed by the experiments of BUISSON and FABRY[1] on the emission of helium, krypton, and neon in GEISSLER tubes. These observations show at the same time that in these rarefied gases there are no resistances whose coefficient does not fulfil the condition (18), and which, acting by themselves, would therefore give rise to a width comparable with that arising from molecular motion, or greater than it. If there had been resistances of this kind, the observed width would have been found greater than is required by DOPPLER's principle.

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[1] H. BUISSON et CH. FABRY, La largeur des raies spectrales et la théorie ciné tique des gaz, Journal de Physique (5) 2 (1912), p. 442.

§ 7. We shall now pass on to consider the influence of molecular motion on an absorption line. We shall suppose that there is a radiation resistance only, or at any rate that there are only resistances whose coefficients g are much smaller than $mn_0 \dfrac{u}{c}$ so that, acting by themselves, they would produce a much smaller width than the one we calculated in § 6. Cases of somewhat greater density are hereby excluded.

The problem is easily solved if, after having grouped the molecules according to their velocity of translation, we substitute for each group a proper value of n_0 in the expression for the electric moment and then take the sum over all the groups in the way shown in equation (3).

Let ξ be the velocity of translation of a molecule in the direction of the beam of light and let one of the groups contain particles with velocities between ξ and $\xi + d\xi$. In (3) we must then replace N by (16) or (17). Further it is clear that the particles in question will resonate with light of the frequency $n_0 \left(1 + \dfrac{\xi}{c} \right) = n_0 \left(1 + \omega \right)$ in the same way as they would with light of the frequency n_0 if they had no velocity of translation. We therefore write $n_0 (1 + \omega)$ instead of n_0. We shall also put

$$n = n_0 (1 + v) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

so that v determines the difference between the frequency of the incident light and n_0, and we shall confine ourselves to small values of v, as we may do in the case of narrow lines. Then, for small values of ω, the only ones for which (17) has an appreciable magnitude, we may write

$$[n_0(1+\omega)]^2 - n^2 = 2n_0^2(\omega - v).$$

Moreover, since n will differ very little from n_0 we may in the term ing replace n by n_0 and consider g as a constant, though in reality this coefficient may depend on n (as g_1 does according to (11)).

Putting further

$$\frac{g}{2mn_0} = k . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

we find

$$(u)^2 = 1 + \frac{1}{2} \sqrt{\frac{3}{2\pi} \frac{N c e^2}{m u n_0^2}} \int_{-\infty}^{+\infty} e^{-\frac{3c^2}{2u^2} \omega^2} \frac{d\omega}{\omega - v + ik},$$

or, if we introduce

$$w = \omega - v$$

as a new variable and put

$$\sqrt{\frac{3}{2}} \cdot \frac{c}{u} = q, \quad \ldots \ldots \quad (21)$$

$$(\mu)^2 = 1 + \frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot \frac{N c e^2}{m u n_0{}^2}(P - iQ), \quad \ldots \quad (22)$$

where

$$P = \int_{-\infty}^{+\infty} \frac{w}{w^2 + k^2} e^{-q^2(w+\nu)^2} \, dw,$$

and

$$Q = k \int_{-\infty}^{+\infty} \frac{1}{w^2 + k^2} e^{-q^2(w+\nu)^2} \, dw.$$

We observe that these formulae determine the indices of refraction and of absorption for light whose frequency is given by (19).

§ 8 We may now avail ourselves of the circumstance that, according to (20), (21) and the inequality (18), which we suppose to hold for g,

$$kq \ll 1 \quad \ldots \ldots \ldots \quad (23)$$

In the first place we find by a simple transformation

$$P = \int_{0}^{\infty} \frac{w}{w^2 + k^2} \{e^{-q^2(w+\nu)^2} - e^{-q^2(w-\nu)^2}\} \, dw,$$

showing that $P = 0$ for $\nu = -\infty$, $\nu = 0$ and $\nu = +\infty$, that the sign of P is always opposite to that of ν, and that $P(-\nu) = -P(+\nu)$. We have therefore only to consider positive values of ν. For these the absolute value of P lies beneath

$$R = \int_{0}^{\infty} \frac{1}{w} \{e^{-q^2(w-\nu)^2} - e^{-q^2(w+\nu)^2}\} \, dw,$$

or

$$R = e^{-q^2\nu^2} \int_{0}^{\infty} \frac{1}{w} e^{-q^2 w^2} \{e^{2q^2\nu w} - e^{-2q^2\nu w}\} \, dw.$$

Developing

$$e^{2q^2\nu w} - e^{-2q^2\nu w}$$

in a series according to the ascending powers of $2q^2\nu w$ and integrating each term separately we find

$$R = 2\sqrt{\pi x}\cdot e^{-x}\left(1 + \sum_{\nu=1}^{\nu=\infty} \frac{1}{(2x+1).x!}x^\nu\right),$$

where

$$x = q^2 v^2.$$

The expression R has a maximum for $x = 0.83$.

This greatest value is 1.92, so that in all cases

$$|P| < 1{,}92 .$$

The integral Q can be evaluated by remarking that the fraction $\frac{1}{w^2+k^2}$ is a maximum for $w = 0$ and becomes very much smaller than this maximum when the absolute value of w exceeds a certain limit w_1, which is a moderate multiple of k. The interval $(-w_1, +w_1)$ therefore contributes by far the greater part to the value of Q. Now, in this interval, as is shown by the inequality (23), the function

$$e^{-q^2(w+v)^2}$$

differs very little from the value

$$e^{-q^2 v^2},$$

corresponding to $w = 0$. We may therefore write

$$Q = k\, e^{-q^2 v^2}\int_{-\infty}^{+\infty} \frac{dw}{w^2+k^2} = \pi\, e^{-q^2 v^2}.$$

It is remarkable that k, and therefore the coefficient g have disappeared from the result.

We see by these considerations that P is smaller than the highest value of Q. Thus, if even for that highest value of Q the factor of i in (22) is small compared with unity, this will also be true of

$$\frac{1}{2}\sqrt{\frac{3}{2\pi}\frac{N c\, e^2}{m\, u\, n_0^2}}\, P ;$$

we may then deduce from (22)

$$(\mu) = 1 + \frac{1}{4}\sqrt{\frac{3}{2\pi}\frac{N c\, e^2}{m\, u\, n_0^2}}(P - i\, Q).$$

Combining this with (4), we find, first the value of the real index of refraction, which we shall not now consider, and secondly that of the index of absorption h, viz. (if in (4) too we replace n by n_0)

$$h = \frac{1}{4}\sqrt{\frac{3}{2}\pi\frac{N e^2}{m\, u\, n_0}}\, e^{-q^2 v^2},$$

or

$$h = h_0\, e^{-\frac{3 c^2}{2u^2}v^2}, \quad \ldots \qquad \ldots \ldots \quad (24)$$

if

$$h_0 = \frac{1}{4} \sqrt{\frac{3}{2}\pi \frac{N e^2}{m u n_0}} \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (25)$$

This is the maximum value of the index of absorption which is found at the middle of the line ($v = 0$).

Whether the supposition that the coefficient of i in (22) is much smaller than unity be right, may be decided by calculating h_0. For it is evident that this supposition is equivalent to the inequality

$$h_0 \lambda_0 \lll 1;$$

it requires therefore that the absorption over a distance of one wave-length is small.

If this is not the case we may not use (24). However, by combining (22) and (4), we then find

$$h = \frac{h_0}{\mu} e^{-\frac{3c^2}{2u^2} v^2},$$

where μ may differ considerably from 1, and h_0 still has the value determined by (25). (This will however no longer be the index of absorption for $v = 0$.)

Formula (25) may be so transformed that it becomes fit for numerical calculation. If we express u in the absolute temperature T and the molecular weight M of the gas, N in T and the pressure p (in mm. of mercury), n_0 in the wave-length λ_0 (in Å.U.), substituting also the values for e and m, we find

$$h_0 = 5,7 \cdot 10^4 p \lambda_0 \sqrt{\frac{M}{T^3}} \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (26)$$

We shall now make some applications of these results.

§ 9. Wood's remarkable experiments[1]) on the scattering of the rays of the ultraviolet mercury line $\lambda 2536$ by mercury vapour have shown that even at ordinary temperatures this scattering is very considerable. The intensity of the beam decreases to half its original value over a distance of 5 mm.

The vapour pressure at this temperature is about $p = 0,001$ and putting $M = 200$ and $T = 290$ I find from (26) a value a little above 400 for h_0. This is much too high compared with Wood's result. It must however be borne in mind that the beam for which he measured the extinction contained a small interval of frequencies, so that we are concerned, not only with the value of h_0, but also with those of h which correspond to small positive and negative values of v and may be considerably smaller than h_0. However,

[1]) R. W. Wood, Selective reflexion, scattering and absorption by resonating gas-molecules, Phil. Mag. (6) 23 (1912), p. 689.

since WOOD has found the scattered rays to be unpolarized, I am rather doubtful as to the propriety of applying the above theory to his experiments. For this reason, I shall no longer dwell on this question.[1]) I shall only add that the value h_0 which we found, leads to a value of $h_0\lambda_0$ considerably below 1.

§ 10. The formulae (24) and (25) may also be used for calculating the total absorption, integrated over the whole width of the line, for a certain thickness of a given gas. On the other hand this absorption can be measured by a simple photometric experiment. Dr. G. J. ELIAS was so kind as to do this for iodine vapour.

A beam of yellow light was passed through an evacuated tube containing some small iodine crystals and heated to 89° C. The beam was obtained by isolating from the spectrum of an arc lamp a portion corresponding to the distance between the D lines. In a layer of 2 cm. the absorption amounted to 15 %.

In discussing this result, I shall remark in the first place that the distribution of light in an absorption band will depend on different circumstances, e g. on the thickness of the gas traversed. It may be that at the middle of the line and within a certain distance from it practically all light is absorbed, the absorption diminishing gradually on both sides. However this may be, one can always define a certain width $\Delta \lambda_e$ such that the amount of light absorbed by the gas is equal to the quantity of light that is found in the incident rays within the interval $\Delta \lambda_e$. The magnitude of $\Delta \lambda_e$, which we may call the "effective" width of the line, can be immediately deduced from a photometric measurement.

The absorption spectrum of iodine vapour has a very complicated structure, containing somewhat over 100 lines between the D lines. Dr. ELIAS's observation shows that the effective widths of all these lines taken together amount to 15% of the distance between the D lines, i.e. to 0,9 Å.U. We shall therefore not be far from the mark if for one line we put on an average

$$\Delta \lambda_e = 0.008 \text{ Å.}U.$$

If $I\,d\lambda$ is the intensity of the incident light within the interval $d\lambda$, we have for the absorption over the whole width of a line by a layer of thickness δ

$$I \int (1 - e^{-2h\delta})\, d\lambda.$$

[1]) According to more recent measurements by A. v. MALINOWSKY (Resonanz-strahlung des Quecksilberdampfes, Ann. d. Physik 44 (1914), p. 935) $h_0 = 1,55$.

Hence

$$\int (1-e^{-2h\delta})\, d\lambda = \Delta\lambda_e,$$

by which we can calculate the maximum absorption index h_0.

For this purpose we develop $e^{-2h\delta}$ in a series and integrate between the limits $v = -\infty$ and $v = +\infty$, after having substituted for h the value (24) and replaced $d\lambda$ by $\lambda_0\, dv$. Putting

$$2h_0\delta = x$$

we find

$$\sum_{x=1}^{v=\infty} \frac{(-1)^{v-1}}{x!\sqrt{x}} x^v = \sqrt{\frac{3}{2\pi}} \cdot \frac{c}{u}\frac{\Delta\lambda_e}{\lambda_0}.$$

With the values $u = 1{,}88.10^4$ cm/sec and $\lambda_0 = 5893$ Å. U. the quantity on the right hand side of this equation becomes 1,50 and we find

$$x = 2h_0\delta = 4{,}1$$

approximately, showing that the absorption at the middle of the line must have been more than $98^\circ/_0$. As $\delta = 2$ cm., the index of absorption itself is found to be about

$$h_0 = 1{,}02\ ^1/_{cm}.$$

§ 11. Now this value is widely different from the one that follows from (26). At 89° C. the pressure of iodine vapour is about 24 mm. Using this value and putting $\lambda_0 = 5893$ Å.U., $T = 362$, $M = 254$, we get from (26)

$$h_0 = 1{,}9 . 10^7\ ^1/_{cm}.$$

The great difference between this number and the former one may be accounted for by supposing that a very small part (about one twenty millionth) only of the molecules are active in producing the absorption, so far as one line is concerned, a conclusion agreeing with that to which one has been led by other lines of research.

It must however be remarked that perhaps the fundamental supposition expressed in equation (1) does not correspond to reality and must be replaced by a more general one. Instead of thinking of a vibrating negative electron we may simply suppose that under the influence of the incident light an alternating electric moment $\mathbf{p}$ is induced in a particle. Equation (1) then takes the form

$$\ddot{\mathbf{p}} + \alpha\dot{\mathbf{p}} + \beta\mathbf{p} = \gamma\mathbf{E}$$

in which α, β, and γ are certain constants, the first of which determines the resistance, while β has the value n_0^2. We are again led to equation (24), but instead of (25) we get an expression which

contains γ. Of this coefficient we can say nothing without making special hypotheses.

§ 12. Finally we shall shortly discuss the question whether the width of FRAUNHOFER's lines in the spectrum of the sun can teach us something about the quantity of the absorbing vapour which produces them. Let us consider an arbitrarily chosen rather fine line, the calcium line λ 5868. Its width is certainly smaller than 0,1 Å.U., by which I mean that, 0,05 Å.U. from the middle, the intensity of the light amounts to more than the part $\dfrac{1}{e}$ of that which is seen at a small distance from the line and which would exist in the place of the line itself if no calcium vapour were present.

If d is the thickness of the traversed layer of calcium vapour we may write, giving to v the value that corresponds to the above mentioned distance of 0,05 Å.U.

$$2hd < 1 ,$$

so that

$$h_0 d < \tfrac{1}{2} e^{\frac{3c^2}{2u^2}v^2} .$$

We can calculate the right hand side of this inequality if we make an assumption concerning the temperature T of the absorbing layer. For $T = 6000°$ we find in this way $h_0 d < 7,0$ and for $T = 3000°$ $h_0 d < 98$.

Now, if it were allowed to use the formula (26), this upper limit for $h_0 d$ would lead to a similar one for pd. We should have for $T = 6000°$, $pd < 0,0015$ and for $T = 3000°$, $pd < 0,0074$. As p represents the pressure expressed in mm. of mercury, whereas d is expressed in cm., we might infer from these numbers that the quantity of calcium vapour, which produces the line in question is very small. Some reserve however must be made here. It may very well be that a small part only of the calcium atoms take part in the absorption. Then the above inequalities will still hold, provided we understand by p the pressure of the "active" vapour. If we mean by p the total pressure of the calcium vapour present we should have to multiply the given numbers by 10^7, if one ten millionth part of the atoms were active (comp. § 11). For the first temperature this would give $pd < 15000$ and for the second $pd < 74000$. The last of these numbers corresponds e. g. to a thickness of 0.75 km. if the pressure is 1 mm. of mercury.

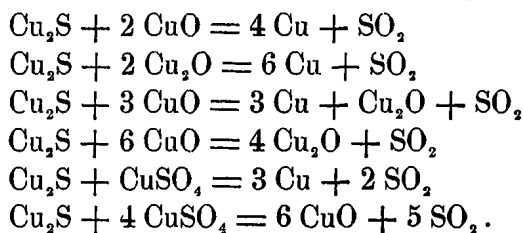If we wish to abstain from all suppositions on the nature of the

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· vibrating particles (comp. the end of the preceding §) we can say
nothing about $p\sigma$ and must confine ourselves to a conclusion con-
cerning $h_0\sigma$. However this may be, it seems rather probable that
the finest lines in the spectrum of the sun are caused by relatively
small quantities of the absorbing gases.

It ought also to be remarked that the problem is, strictly speaking,
less simple than we have put it here. We have reasoned as if a small
quantity of an absorbing vapour were present in front of a radiating
body giving rise to a continuous spectrum. In this spectrum there will
then be a fine absorption line. In reality, however, if there is very
rare calcium vapour in a certain layer, there will be vapour of
somewhat greater density at a greater depth in the sun's atmosphere.
For a satisfactory theory of the phenomena it would be necessary
to explain why this latter vapour does not give rise to a broader
absorption line, but must rather be considered as belonging to the
mass to which the continuous spectrum is due.

Chemistry. — *"Equilibria in the system $Cu—S—O$; the roasting
reaction process with copper."* By Prof. W. REINDERS and
F. GOUDRIAAN. (Communicated by Prof. HOOGEWERFF).

(Communicated in the meeting of May 29, 1915.)

1. In the metallurgy of copper the reactions, which may occur
between the roasting products of the partly burnt copper ore, play
an important role; in special conditions they can lead in a direct
manner to the separation of metal. Usually it is assumed that these
reactions take place according to the subjoined equations [1]:

$$Cu_2S + 2\,CuO = 4\,Cu + SO_2$$
$$Cu_2S + 2\,Cu_2O = 6\,Cu + SO_2$$
$$Cu_2S + 3\,CuO = 3\,Cu + Cu_2O + SO_2$$
$$Cu_2S + 6\,CuO = 4\,Cu_2O + SO_2$$
$$Cu_2S + CuSO_4 = 3\,Cu + 2\,SO_2$$
$$Cu_2S + 4\,CuSO_4 = 6\,CuO + 5\,SO_2.$$

Systematic researches as to this process, which seems very com-
plicated owing to the large number of possible phases, are exceedingly
scarce. The only observations worth mentioning are those of R.
SCHENCK and W. HEMPELMANN [2]; they determined pT-lines for mixtures
of $Cu_2S—Cu_2O$, $Cu_2S—CuSO_4$ and $Cu—CuSO_4$. As these observations
are incomplete and their conclusions in many points unsatisfactory,

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[1] SCHNABEL, Handb. der Metallhüttenkunde I 176 (1901).

[2] Metall und Erz, 1, 283 (1913). Z. f. angew. Chemie 26, 646 (1913).