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ON THE BROADENING OF SPECTRAL LINES.

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TO ACCOUNT for the finite width of the spectral lines of a substance emitting approximately homogeneous radiations, the following hypotheses have been proposed:

1. As a consequence of Kirchhoff's law "the ratio of brightness of two immediately contiguous portions of a discontinuous, bright-line spectrum constantly decreases, if the number of luminous strata is multiplied or if the coefficient of absorption of the single stratum is increased, until the value is reached which, for the same wave-length and the same temperature, corresponds to the ratio in the continuous spectrum of a body completely opaque for the given thickness."[1]

2. The direct modification of the period of the vibrating atoms in consequence of presence of neighboring molecules.

3. The exponential diminution in amplitude of the vibrations due to communication of energy to the surrounding medium, or to other causes.

4. The change in wave-length due to the Doppler effect of the component of the velocity of the vibrating atom in the line of sight.

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[1] SCHEINER, *Ast. Spect.*

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To these the following causes may be added:

5. The limitation of the number of regular vibrations by more or less abrupt changes of phase amplitude or plane of vibration, caused by collisions.

6. The possible variations in the properties of the atoms within such narrow limits as to escape detection by other than spectroscopic observations.

This last hypothesis is added chiefly for the sake of completeness, but it seems highly improbable that this cause could be of great importance, and serious objections at once occur, if we attempt by its means to explain the effects of temperature and pressure.

The most promising method of assigning to these different causes their proper measure of importance is to investigate such effects of temperature and pressure from the theoretical as well as the experimental side, and until this is accomplished only vague and unsatisfactory conclusions may be expected. The great importance of such a study, and the interest in it which is shown by such able contributions as those of Wiedeman, Ebert, Rayleigh, and recently, of Jaumann and Galitzin justify the prediction that a complete and satisfactory theory will be forthcoming in the near future.

Meanwhile it may be of interest to consider some results which have been reached in the present paper as a result of several months' labor. That these are in some cases very imperfect is freely admitted, but it is hoped that further experiment may give more definite information—and at least that this contribution will present the essential points in such a manner as to open the work to discussion and criticism.

The objections to the hypotheses numbered 1 and 3 have been considered by Galitzin, Kayser, and others, and these are, I believe, fatal unless the main contention that they are the essential causes be abandoned. Very probably they produce secondary effects which may be traced when the complete theory is developed.

In regard to 4, I cannot agree with the conclusions of Galitzin.

On the contrary the evidence of a very large number of experiments points unmistakably to effects of motion of the molecule in the line of sight. Lord Rayleigh[1] has shown from the standpoint of the kinetic theory that the motion of the molecule in the line of sight can produce a broadening of the lines, and it seems probable that this is the chief if not the only effective cause in operation when the density of the radiating body is low.

Thus in the case of hydrogen it has been shown that the increase in width of the red line above its width at zero pressure is proportional to the pressure,[2] but that even at zero pressure (pressures below $0^{mm}.5$) it has a definite width which is of the order of magnitude required by Rayleigh's investigation on the assumption of a molecular velocity of from 2000 to 4000 meters per second. It has also been pointed out that this limiting width of the spectral lines on this assumption should be proportional to the square root of the absolute temperature and inversely proportional to the square root of the molecular weight of the radiating substance.

The following table gives a list of substances of molecular weights varying from 1 to 200 v_1 and v_2 denote molecular velocities, the former deduced from the inverse ratios of the square root of the molecular weight; the latter calculated from the visibility curves. The agreement with theory while far from perfect is still—considering the difficulties of the experiments, and especially the uncertainty in the temperatures—too striking to be accidental.

It may therefore be conceded that while the causes 1, 3, 4 and 6 together or separately may and probably do produce an appreciable effect, they are generally insufficient to account for the broadening of the spectral lines.

[1] *Phil. Mag.*, April, 1889.

[2] *Phil. Mag.*, September, 1892.

Substance	At. Wt.	v_1	v_2
Hydrogen	1	2000	1500
Lithium	7	800	1200
Oxygen	16	500	800
Sodium	23	400	400
Magnesium	24	400	650
Iron	56	260	500
Cobalt	59	260	560
Nickel	59	260	500
Copper	63	250	450
Zinc	65	250	450
Palladium	106	190	250
Silver	108	190	250
Cadmium	112	190	220
Gold	196	140	225
Mercury	200	140	140
Thallium	204	140	110
Bismuth	210	140	150

The following is an attempt to deduce the value of the broadening of the spectral lines (or at least to find its order of magnitude) on the hypothesis 5.

In Fourier's formula,

$$\phi(x)=\frac{1}{\pi}\int_0^\infty du\,(C\cos ux+S\sin ux),$$

in which

$$C=\int_{-\infty}^{\infty}\phi(v)\cos uv\,dv \quad\text{and}\quad S=\int_{-\infty}^{+\infty}\phi(v)\sin uv\,dv,$$

the second member represents a group of perfectly homogeneous trains of waves.

If therefore $\phi(x)$ represents the train of waves incident on a prism, the intensity of its spectrum will be

$$\psi^2(u)=C^2+S^2.$$

Suppose the incident light to consist of a limited number of exactly equal waves corresponding to the number of vibrations emitted by the molecule between two collisions.

If ρ = free path of the molecule,
v = velocity of translation,
V = velocity of light,
r = length of a single train of waves,

then, between the limits $-\frac{1}{2}r$ and $\frac{1}{2}r$ we have

$$\phi(x) = a \cos m x + b \sin m x$$

$$C = a\int_{-\frac{r}{2}}^{+\frac{r}{2}} \cos mv \ \cos uv \ dv = a\,\frac{\sin\frac{1}{2}(m-u)r}{m-u} + a\,\frac{\sin\frac{1}{2}(m+u)r}{m+u}$$

$$S = b\int_{-\frac{r}{2}}^{+\frac{r}{2}} \sin mv \ \sin uv \ dv = b\,\frac{\sin\frac{1}{2}(m-u)r}{m-u} - b\,\frac{\sin\frac{1}{2}(m+u)r}{m+u}$$

These terms are all very small (since m is large) except for values of u which differ but little from m or from $-m$. Leaving negative values of u out of consideration, and replacing $u-m$ by $2\pi n$ we have

$$\psi^2(n) = \frac{(a^2+b^2)}{4}\,\frac{\sin^2\pi n r}{\pi^2 n^2}$$

This represents the distribution of intensities in the spectrum of such a limited train of waves, and if the free path and the velocities of all the molecules were the same, the "width" of the resulting spectral line might be obtained from this expression.

Fig. 1 represents the intensity curve, and the "width" of the line may be taken equal to

$$\pi n r = \pi, \text{ whence}$$

$$n = \frac{1}{r} = \frac{1}{\rho}\,\frac{v}{V}, \text{ or in wave-lengths,}$$

$$\delta_2 = n\lambda^2 = \frac{\lambda^2}{\rho}\,\frac{v}{V}.$$

In the case of hydrogen at a pressure of 100 mm. we may take $\lambda = 6560 \times 10^{-10}$ $v = 3000$ $V = 3 \times 10^8$ $\rho = 7500 \times 10^{-10}$, whence $\delta_2 = .057$ tenth-meter.

The corresponding quantity obtained by experiment (p. 295, *Phil. Mag.*, September 1892) is $2\,(0.128 - 0.048) = 0.16$ tenth meters which is of the same order of magnitude as the theoretical value.

As experiment has shown that in every case thus far examined the width of the spectral lines diminish with the pressure in an approximately linear proportion towards a constant limiting value, we may for a first approximation derive a formula for the actual width of the line on the assumption that this is the sum of the separate widths due (1) to the motion in the line of sight (2) to the limitation of the free path. The latter has just been given. The former is $\frac{2}{\pi} \times \frac{l2}{\Delta}\lambda^2$ if Δ is the distance at which the "visibility curve"[1] falls to half its maximum value.

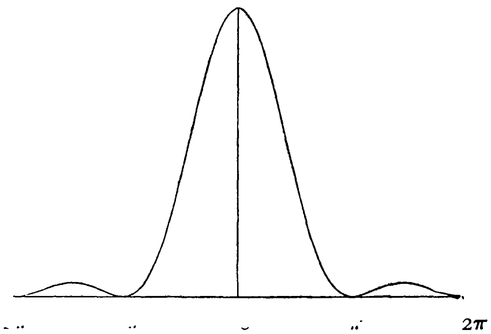

FIG. 1.

Rayleigh's formula as modified by the definition of visibility given in a former paper[2] becomes

$$V = e^{-\pi\left(\frac{\pi X}{\lambda}\frac{v}{V}\right)^{2}}$$

which gives $\Delta = \frac{1}{\pi}\sqrt{\frac{l2}{\pi}\frac{V}{v}}\,\lambda$, whence

$$\delta_1 = 2\sqrt{\pi l 2}\,\frac{v}{V}\lambda = 3\frac{v}{V}\lambda, \text{ nearly.}$$

We have then $\delta = \delta_1 + \delta_2 = \frac{v}{V}\lambda\left(3 + \frac{\lambda}{\rho}\right)$.

If v = molecular velocity at absolute temperature θ and v_0 the corresponding velocity at θ_0, m the molecular weight; d, the actual density and d_0 the standard density, ρ the corresponding length of free path at d_0, formula (1) becomes

$$\delta = \frac{v_0}{V}\frac{\lambda}{\sqrt{\theta_0}}\sqrt{\frac{\theta}{m}}\left(3 + \frac{\lambda}{\phi}\frac{d}{d_0}\right).$$

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[1] *Phil. Mag.*, April, 1891.

[2] *Phil. Mag.*, September, 1892.

In view of the imperfect assumptions it will be better not to attach too much weight to the value of the constants, but it may be worth while to examine the more general formula.

$$\delta = \sqrt{\frac{\theta}{m}}\lambda\,(a + b\lambda d)$$

The experiment verification of this formula is attended with considerable difficulty. Nevertheless the results thus far obtained show that it may be considered as a good first approximation to the truth.

The following are the points which seem to be fairly well established:

1. When the pressure is below one-thousandth of an atmosphere, the second term, $b\lambda d$, may be neglected.

2. Under this condition the width of the line is roughly proportional to the square root of the molecular weight. This is shown in the table.

3. The width increases as the temperature rises, the rate being not very different from that of the square root.

4. When the pressure is increased, the width increases in a nearly linear proportion. (This is shown in Fig. 2, in which the ordinates are widths of line in tenth-meters, and the abcissae are pressures of surrounding gas in mm.)

5. The rate of this increase varies considerably with different substances, but in general it is more rapid, the smaller the molecular weight, and while the actual results can scarcely be said to prove that the rate is inversely as the square root of the molecular weight, they do not differ very greatly from this proportionality.

6. At low pressures the proportionality with λ is not proved—there being about as much evidence for an increaseof δ with λ as for a decrease.

7. At high pressures the width increases with wave-length, but the exact law is not determined.

8. The nature of the surrounding gas or vapor is of secondary importance.

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In regard to cause 2 it may be remarked that at pressures below one atmosphere the length of the free path is of the order of one hundred times the radius of the sphere of action of the molecules. It appears probable therefore that at such pressures the number of free vibrations is also at least one hundred times as many as those whose period is modified by collision, and the effect of these modified vibrations would be correspondingly small in broadening the spectral lines except at great densities.

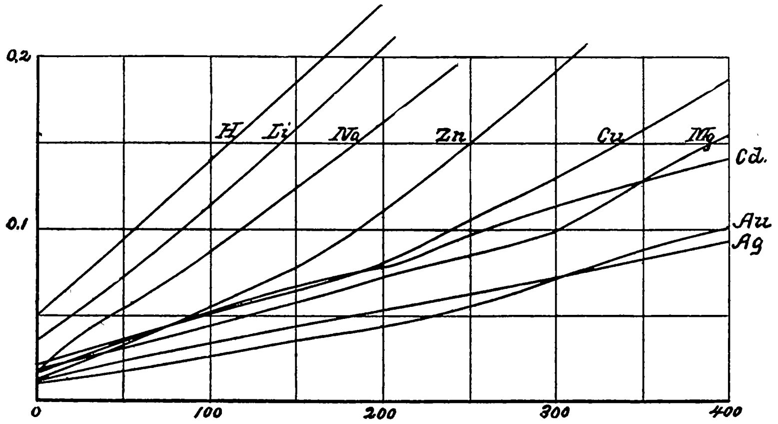

FIG. 2.

It appears probable that the vibratory energy is supplied during "collisions." It does not necessarily follow that the source of this energy is the motion of translation of the molecule (that is, a function of the temperature), but we may suppose, with J. J. Thomson, that there is an interchange of partners among the molecules—which could not occur except on collision—and it seems reasonable to suppose that during this interchange, the chemical (electrical) energy of combination is transformed into electrical vibrations (light).

If we suppose the amplitude of the vibrations to vary as some inverse power of the distance, r, between the approaching molecules we would have

$$\frac{A_0}{A} = \left(\frac{r}{a}\right)^p,$$

A_0 being the amplitude corresponding to the nearest distance a, But it can be shown that the distance e traveled by the molecule when the amplitude has fallen to one-half its maximum value, in the case of hydrogen at 100 mm. pressure, is of the order of a ten thousandth of a millimeter, so that by the preceding equation $a = (\frac{1}{2})^{\frac{1}{p}} \times e$. a is also of this order of magnitude unless p be small. But this is the order of magnitude of the free path of the molecule, and in all probability the nearest approach is hundreds or thousands of times smaller; so that we are forced to conclude either that p is very small—which is only another way of saying that the amplitude is nearly independent of the distance between the molecules; or else that such a variation of intensity is not an important factor in broadening the spectral lines.

This seems at least conclusive for low or moderate densities. On the other hand, for greater densities, it seems not unlikely that the mutual influence of the molecules may be of great importance.

Where the broadening of the lines is unsymmetrical, and especially where the line is terminated at one side by a sharp edge such broadening can be explained by certain assumptions concerning the law of action of the molecules on their rates and intensities of vibration.

Thus, in the preceding illustration, if

$$\phi(x) = \frac{a}{a^2 + x^2} \cos mx + \frac{x}{a^2 + x^2} \sin mx,$$

the resulting intensity of the spectrum is $I = e^{-4\pi a n}$ for positive values of n, and zero for negative values.

If this view is correct, then starting with zero pressure the line should always begin to broaden symmetrically at first, and the assymmetrical broadening should not appear until the pressure is very considerable. As in most cases the width of the spectral lines at low pressure is so small that it is usually masked by imperfections of the spectroscopes employed, this question must be attacked by interference methods.

The method of deducing the form and distribution of light in a spectral line by the visibility curve of its interference fringes has already given very promising results; but if rigorously interpreted, as shown by Lord Rayleigh,[1] it is limited to the case of symmetrical distributions of light in the source. In fact, for an unsymmetrical source we have

$$V=\sqrt{C^2+S^2} \tag{1}$$

which gives, however, no information concerning C or S.

In order to determine these another equation is necessary, and this is furnished by the change of phase. If ϕ is the phase of the interference band we have

$$\tan\phi=\frac{S}{C} \tag{2}$$

These two equations determine S and C, and from them we have by Fourier's theorem

$$\sqrt{I}=\psi(n)=\frac{1}{\pi}\int_0^\infty d\alpha\cos\alpha n\int_{-\infty}^{+\infty}d\lambda\,\psi(\lambda)\cos\alpha\lambda$$
$$+\frac{1}{\pi}\int_0^\infty d\alpha\sin\alpha n\int_{-\infty}^{+\infty}d\lambda\,\psi(\lambda)\sin\alpha\lambda$$
$$\text{or }\psi(n)=\frac{1}{\pi}\int_0^\infty C\cos\alpha n\,d\alpha+\frac{1}{\pi}\int_0^\infty S\sin\alpha n\,d\alpha.$$

At first it would seem that the determination of the "ϕ" curve would be attended with insurmountable difficulties; for it is practically impossible to divide or even to read a scale so accurately as to find directly the difference of phase, which is, of course, but a fraction of a wave-length.

The following method, judging from some preliminary results obtained in the course of the determination of the length of the meter in light-waves,[2] gives promise of furnishing the required solution.

Suppose an "intermediate standard"[2] consisting of two plane parallel surfaces one centimeter apart to be placed in the "interferometer" and circular fringes obtained for both surfaces.

The phase α and α' of the central dark circle for both surfaces is measured by the "compensator," and the standard is

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[1] *Phil. Mag.* November 1892.

[2] Tome XI. *Trav. et Mem. Bur. Int. des Poids et Mésures.*

advanced through its own length and the measurement repeated. If the phase ϕ is constant the difference of phase $\alpha - \alpha'$ will also be constant; if not, then $\phi_n = \Sigma^n{}_1 (\alpha - \alpha') - n (\alpha - \alpha')_0$ provided the change be not too rapid. If this should be the case, a shorter distance-piece or "intermediate standard" must be used, or two standards of different lengths may be used, and the "ϕ" curve determined by the same process as is employed in thermometer calibrations.

The following experiment appears to prove conclusively that the temperature (velocity of translation of the molecule) in the case of the electrical discharge through rarefied hydrogen, must be remarkably low, though it may be premature to say that it is only a few degrees above that of the surrounding atmosphere.

Dry hydrogen, moderately pure at a pressure of about 1 mm. was contained in a vacuum tube made of hard glass whose section varied gradually from 15 mm. to 1 mm.

On the passage of the spark the characteristic spectrum of hydrogen was observed — the brightness increasing as the diameter diminished.

The light was directed into the interferometer, and after interposing a red glass it was found that the interference fringes (conc. circles) were much more clearly visible at a portion of the tube where the diameter was about 4 mm., and this portion was accordingly employed. The tube was then surrounded by a thin roll of sheet copper, except at the part examined, and this was heated by a Bunsen flame. The falling off in distinctness of the fringes was at once visible, and when a thermometer placed in contact with the copper showed a temperature below 300° C., the distance at which interference was still visible was about three-fourths of its value at the lower temperature. If the actual temperature in the first measurement is 50° or about 320° absolute, then the second temperature (supposing that the thermometer indicated — very roughly of course — the increase in temperature) was about 570°. The corresponding ratio of velocities is about $\sqrt{\frac{320}{570}} = \frac{3}{4}$, which agrees with the result of

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experiments. If, on the other hand (as has been assumed by those who believe the temperature to be the efficient cause in producing incandescence), it be supposed that the first temperature was of the order of 7000°, the second could not have been more than 7300° and the corresponding ratio of velocity (and also of difference in path at which interference phenomena are still visible) would be $\sqrt{\frac{7000}{7300}} = .98$, which is so near unity that it would not be possible to detect the change.

Aside from this, the distance at which interference is visible in the case of hydrogen at low pressure is that which corresponds to a velocity of translation of from 2000 to 4000 meters per second; so that even from this measurement alone it would follow that the temperature must be between 0° and 300° C.

Since the pressure of hydrogen vapor in solar prominences (at any rate for the extremity farthest from the Sun's disk) must be extremely low, it follows that the greater part of the width of the corresponding spectral lines must be due chiefly to molecular velocities. Accordingly, an accurate measurement of this width will give the temperature of the prominence.

As the details of the methods by which the preceding experimental results were obtained have not yet been published it may be of interest to describe here the arrangements used for the source of light.

It gives me great pleasure to acknowledge in this connection the valuable assistance of my colleague, Mr. S. W. Stratton.

Many of the experiments were simple modifications of those described in a previous paper and no further notice of them is necessary. For substances whose point of volatilization was higher than the melting point of glass, the following device was employed:

A glass globe *G*, with a funnel-shaped aperture, *F*, closed by a piece of plate glass, is attached to the iron tube *T*, and the enclosed space is connected with a mercury pump, the tube being filled with mercury, forming a barometric column. This permits a long rod to rotate within, thus breaking contact between the disk *W* and the spring *S*. Either *S* or *W* or both are of the material whose spectrum is to be investigated.

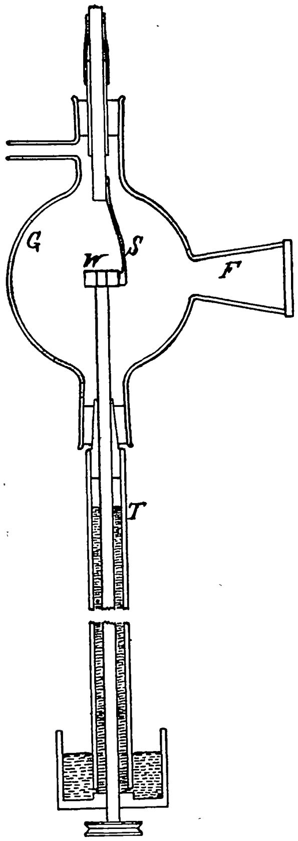

FIG. 3.

The extra-current spark, even with two or three storage cells, and with or without an induction coil, is sufficient to produce a very brilliant light, especially when the pressure within the globe has been reduced to a few millimeters.

Various modifications have been employed, especially one in which the break was produced by a reciprocating instead of a rotary motion. An essential point is to have all the parts readily detachable, so that the globe which rapidly becomes coated with a metallic deposit may occasionally be cleaned.

By constricting the attachment of the funnel at *O* to about 10 mm., the glass plate *P* may remain for days or weeks without cleaning.

It is hoped that future experiments along the lines here indicated may throw new light upon many of the important problems suggested.