STUDIES IN LUMINESCENCE.

VI. THE DECAY OF PHOSPHORESCENCE IN SIDOT BLENDE.[1]

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THE decay of phosphorescence was first studied by E. Becquerel.[2] In the case of short-duration phosphorescence the phosphoroscope was used for this purpose and the intensity of phosphorescence was measured for different speeds of the rotating disc. Becquerel regarded it as probable that the law of decay was of the form

$$I = I_0 e^{-at}, \tag{1}$$

and found that the observations were in fact fairly well represented by an exponential expression. In discussing these observations, however, Becquerel tacitly assumed that no appreciable time was required for the exciting rays to produce their full effect. Later investigations have shown that this assumption is not justified. Since a change in the speed of the phosphoroscope altered not only the time that elapsed between excitation and observation, but also the duration of exposure, it is probable, therefore, that the initial excitation was less at high speeds. Attention was directed to this point by E. Wiedemann and later by H. Becquerel, who states that a recomputation of the data shows a less satisfactory agreement with the exponental law than at first appeared.

For the long-time phosphorescence of the phosphorescent sulphides E. Becquerel proposed an empirical expression of the form

$$I^m(c + t) = cI_0^m. \tag{2}$$

For each of the seven substances tested this expression was found to show a fairly good agreement with the experimental results

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[1] An account of the work described in this paper was presented to the American Physical Society at the meeting held on Oct. 28, 1905. An abstract appeared in the PHYSICAL REVIEW, Vol. XXI., p. 411, December, 1905.

[2] Becquerel, "La Lumière." See also Comptes Rendus, Vol. 51, p. 921, 1860, and Annales de Chimie et de Physique, Series 4, Vol. 62, p. 5.

throughout a considerable range. In one case, namely that of a calcium sulphide preparation giving an orange-red phosphorescence, the expression represented the observations with considerable accuracy throughout the whole range, the value of m being 0.5. But in most cases it was not possible to find values of m and c which would make the formula fit the experimental data for the whole time of decay. The values of m that suited the observations best lay between 0.5, for the calcium sulphide just mentioned, and 0.806 for another calcium sulphide having an orange yellow phosphorescence.

The same empirical formula has since been very generally used; among others by Darwin[1] in 1881, and Ch. Henry[2] in 1892. The former worked with Balmain's paint and found the best value for m to be 0.86. It cannot be said, however, that the experimental results were represented very accurately by the formula. The substance used by Henry was Sidot's blende, several different samples of which were tested. Henry states that in the case of one specimen the results were represented by an exponential law (eq. 1) for 14 seconds, while other preparations obeyed the law

$$i^{0.5936}(t + 27.18) = 1,647.5 \tag{3}$$

Henry appears to have been convinced of the corrections of the latter law and proposed a new type of photometer which made use of the gradually decaying phosphorescence of Sidot blende in the measurement of faint sources of light.[3] While the fact that the constant in eq. (3) is given to five significant figures indicates an accuracy that is unusual in photometric measurements, the lack of experimental data in the paper referred to makes it difficult to form an independent opinion of the significance of the conclusions.

The decay of phosphorescence was considered from the theoretical standpoint by H. Becquerel[4] in 1891. Upon the assumption that the light emitted during phosphorescence was due to molecular vibrations set up by the action of the exciting light and afterwards gradually dying out, it was shown that the law of decay would be

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[1] Philosophical Magazine, Vol. 11, p. 209, 1881.

[2] Comptes Rendus, Vol. 115, p. 505, 1892.

[3] Comptes Rendus, Vol. 115, p. 602.

[4] Comptes Rendus, Vol. 113, p. 618, 1891.

determined by the nature of the damping forces. If the vibrations meet with an opposing force proportioned to the speed it was shown that an exponential law of decadence would result; while if the resistance is proportional to the square of the speed the law of decadence would take the form

$$I = \frac{1}{(a + bt)^2}. \qquad (4)$$

It will be noticed that the emprical law proposed by E. Becquerel reduces to (4) in case $m = 0.5$.

In the case of a substance whose phosphorescent spectrum contains several bands Becquerel proposed the expression

$$I = \Sigma \frac{1}{(a + bt)^2}, \qquad (5)$$

in which there is one term in the summation for each band. Upon testing this law with the data obtained by E. Becquerel for a calcium sulphide giving blue phosphorescence it was found that the results could be expressed by the use of two terms in the above series with great accuracy. The existence in the spectrum of this substance of two bands possessing independent properties could be demonstrated in various ways.

In the derivation of the law proposed by H. Becquerel the assumption is that the vibrations set up by the action of the exciting light continue during several minutes or even hours. This would imply either that the vibrating atoms or molecules exist during this time without collisions with other molecules, or else that such collisions are without effect upon the vibrations. Neither of these suppositions seems to us tenable. But the law nevertheless appears to be of very general application. We shall show later that the same law may be derived from entirely different theoretical considerations.

In all of the experiments upon the decay of phosphorescence with which we are familiar it is the total light that has been measured; so far as we are aware no attempt has been made to determine the law of decay for different portions of the phosphorescence spectrum. This fact complicates the problem greatly, for in most cases of phosphorescence the spectrum consists of two or more bands, which, in general, decay at different rates. It can hardly be expected, therefore, that measurements of the total light will be found to obey a simple law. The difficulties resulting from the complexity of the luminescence spectrum were recognized by E. Becquerel and were several times mentioned in the course of his classic researches. In discussing his experiments on decadence he suggested an expression of the form

$$I = Ae^{-\alpha t} + Be^{-\beta t} + \cdots \tag{6}$$

for the intensity of the total phosphorescence, with one term for each band in the spectrum. But the difficulties of computation were such as to lead him to abandon this expression and to employ instead the empirical expression of eq. (2). Recognition of the fact that each band has its own rate of decay is also implied in the law proposed by H. Becquerel (eq. 4).

EXPERIMENTAL.

While it is possible to test the corrections an expression of the form of (4) or (6) by comparison with measurements of total intensity, such a test is difficult, and cannot be altogether satisfactory; for with an expression containing several terms the number of constants is so great that the law may be made to fit almost any data. It is clear that a much more severe test of any given law of decay may be obtained from experiments with a substance having only one band in its phosphorescence spectrum. The Sidot blende screen used by us in earlier experiments[1] was found to have three bands in its luminescence spectrum. But since the two violet bands do not appreciably overlap the green band the spectrophotometer enables the behavior of the latter band alone to be conveniently studied. The matter is still further simplified by using the violet rays of the arc in excitation, since these rays, while they produce a brilliant green luminescence, are incapable of exciting either one of the violet bands.[1] In view of the brilliancy of the green band, its long duration, and the ease in which it may be isolated, this band seems well adapted to the study of the decay of phosphorescence.

Our previous experiments on Sidot blende have shown that in the case of the green band the phosphorescence spectrum shows no

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[1] Physical Review, Vol. XXI., p. 247, 1905.

measurable change in form during the first ten seconds of decay. In other words, the rate of decay is the same for all wave-lengths. To fix the behavior of the whole band it would be sufficient, therefore, to determine the law for a single wave-length. We have, however, made measurements at three different wave lengths, namely, at 0.483 μ, 0.512 μ and 0.547 μ. The first of these wave-lengths lies near the ultra edge of the band; the second is not far from the maximum; and the third is near the red edge.

The methods of measurement were the same as those described in our last paper.[1] The experimental data obtained are contained in the following three tables. In each case it is the average of from ten to twenty observations that is recorded.

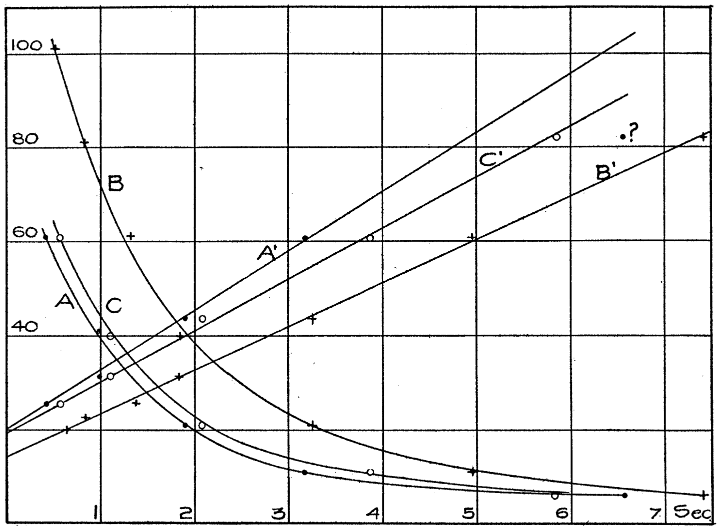

Fig. 36. Curves A, B and C show the decay in the phosphorescence of Sidot blende for the wave-length 0.483 μ, 0.512 μ and 0.547 μ, respectively. The curves A', B' and C' are obtained from A, B and C by plotting $I^{-\frac{1}{2}}$ instead of the intensity of phosphorescence, I.

In the set of observations contained in Table I. the curves for 0.547 μ, 0.483 μ and 0.512 μ were determined during the forenoon in the order just stated. The data for 0.512 μ with weaker excitation were observed during the afternoon of the same day.

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[1] Physical Review, Vol. XXI., p. 247, 1905.

The observations recorded in Table II. were taken in a different manner, the measurements at a given intensity being made for each of the three wave-lengths in succession. The observations of December 13 (Table III.) were made in a similar manner. The first three curves of Table I. are plotted in Fig. 36, while the second and fourth curves of this table are shown in Fig. 37.

TABLE I. [NOV. 25.]

Time in Seconds Required for the Phosphorescence to Fall from its Initial Intensity to the Intensity I. The Computed Values of t are Derived by Substitution in the Following Equations:

For $\lambda = 0.483\,\mu$ $1/\sqrt{I} = 0.102 + 0.059\,t$
$\lambda = 0.512\,\mu$ $1/\sqrt{I} = 0.074 + 0.045\,t$
$\lambda = 0.547\,\mu$ $1/\sqrt{I} = 0.096 + 0.055\,t$
$\lambda = 0.512\,\mu$ (weaker excitation) $1/\sqrt{I} = 0.092 + 0.052\,t$

I	$\lambda = 0.483\,\mu$		$\lambda = 0.512\,\mu$		$\lambda = 0.547\,\mu$		$\lambda = 0.512\,\mu$ Weaker Excitation.	
	t sec. Obs.	t sec. Comp.	t sec. Obs.	t sec. Comp.	t sec. Obs.	t sec. Comp.	t sec. Obs.	t sec. Comp.
101			0.63	0.58				
81			0.83	0.85				
61	0.41	0.44	1.38	1.20	0.56	0.58	0.72	0.69
41	0.99	0.92	1.84	1.83	1.10	1.09	1.24	1.23
21	1.88	1.98	3.25	3.23	2.07	2.23	2.42	2.45
11	3.16	3.39	4.95	5.10	3.87	3.74	4.03	4.04
6	6.55	5.23	7.42	7.50	5.82	5.71	6.22	6.92

TABLE II. [DEC. 10.]

Time in Seconds Required for the Phosphorescence to Fall to the Intensity I. The Computed Values of t are Derived by Substitution in the Following Equations:

For $\lambda = 0.512\,\mu$ $1/\sqrt{I} = 0.078 + 0.034\,t$ $\lambda = 0.547\,\mu$ $1/\sqrt{I} = 0.104 + 0.042\,t$

I	$\lambda = 0.483\,\mu$		$\lambda = 0.512\,\mu$		$\lambda = 0.547\,\mu$	
	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.
81.4	0.60		1.06	0.98	0.30	0.22
61.4	0.77		1.35	1.49	0.55	0.62
31.4	2.40		2.98	3.02	1.83	1.84
11.4	4.13		6.47	6.46	4.62	4.58

TABLE III. [DEC. 13.]

Time in Seconds Required for the Phosphorescence to Fall to the Intensity I. The Computed Values of t are Derived by Substitution in the Following Equations :

For $\lambda = 0.483\,\mu$ $1/\sqrt{I} = 0.104 + 0.070\,t$

$\lambda = 0.512\,\mu$ $1/\sqrt{I} = 0.094 + 0.046\,t$

$\lambda = 0.547\,\mu$ $1/\sqrt{I} = 0.118 + 0.070\,t$

I	$\lambda = 0.483\,\mu$		$\lambda = 0.512\,\mu$		$\lambda = 0.547\,\mu$	
	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.
81.4			0.45	0.37		
61.4	0.45	0.36	0.69	0.74	0.25	0.14
31.4	1.06	1.08			0.88	0.87
21.4	1.46	1.61	2.60	2.67	1.30	1.40
11.4	2.78	2.76	4.48	4.44	2.61	2.55
7.4	4.46	3.80	5.97	6.00	4.58	3.57

The data of the preceding tables have been used to test the applicability of each of the several proposed laws of decay to the case of a single band. It was found that the results can be closely represented by an expression of the form given in eq. (4). To determine the constants a and b of this equation a convenient graphical method was employed, in which the values of $1/\sqrt{I}$ were plotted as ordinates and times as abscissas. Since eq. (4) may be written in the form

$$\frac{1}{\sqrt{I}} = a + bt,$$

the points located in this manner should lie on a straight line. A straight line having been drawn as nearly as possible through all the points, the slant of this line and its y intercept at once gave the values of b and a respectively. The values of a and b determined in this way are given in each of the tables, and the values of t computed from the above equation are tabulated for comparison with the times observed.

In Figs. 36 and 37 the values of $I^{-\frac{1}{2}}$ have been plotted as described above. It will be noticed that in each case the points lie very nearly upon a straight line, and that there is nothing to indicate any systematic variation from linearity. In the case of one curve, namely that for 0.483 μ in Table II., the points located in this way did not lie even approximately on a straight line. This curve, therefore, does not have the form corresponding to eq. (4). But in the case of the other curves, including one taken at this same wave-length (Table I.), the agreement between the observed and computed values of t is satisfactory, the differences being only such as might well result from accidental errors. It seems probable therefore that the observations at 0.483 μ in Table II. were subject to some unusual source of error.

In Fig. 36 it will be noticed that one point of the line A' (indicated by a question mark) falls below the line, *i. e.*, the observed time of decay was considerably greater than that computed from an assumed linear relation between $I^{-1/2}$ and t. Discrepancies of the same kind will be found for the smallest values of I in the first curve of Table I. and for the first and last curves of Table III. No such discrepancies are present in any of the four curves taken at 0.512 μ — *i. e.*, near the maximum of the phosphorescence spectrum. If these cases of disagreement between the observed and computed values of t are not due to accidental errors,

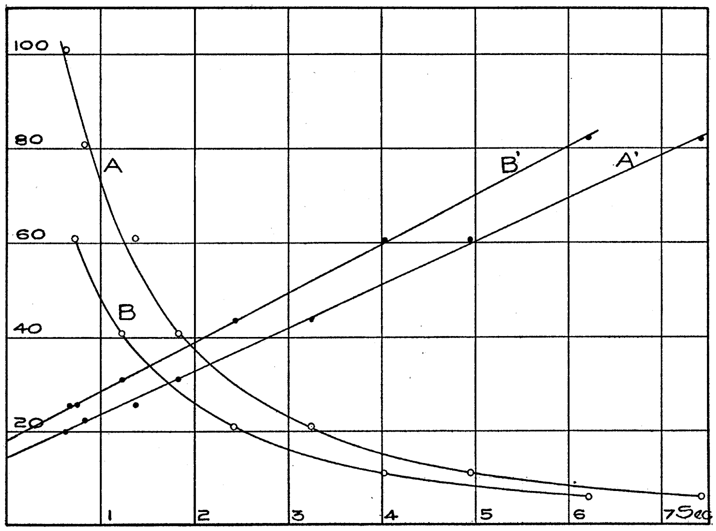

Fig. 37. Curves A and B show the decay of phosphorescence at 0.512 μ for two different intensities of the exciting light. In the curves A' and B' $I^{-\frac{1}{2}}$ is plotted instead of the intensity I.

they show that the violet edge of the phosphorescence band dies out more gradually than the maximum. Our previous observations[1] had indicated that if any difference exists between the two rates, the violet end of the band decays more rapidly than the center. Because of these conflicting indications, and especially because of the difficulties of making accurate readings for small intensities, we are inclined to ascribe the seeming variations from linearity to accidental errors.

Theoretical.

In attempting to interpret the results of the foregoing experiments we have found it useful to consider the subject from the standpoint of a hypothesis first proposed in explanation of luminescence phenomena by E. Wiedemann[2] and later modified and extended by Wiedemann and Schmidt.[3] According to this view some chemical or physical change is produced in a luminescent substance during excitation, and the emission of light is an accompaniment of the more or less gradual restoration of the modified substance to its original condition. Thus, in the case of phosphorescence, it was suggested by Wiedemann that a portion of the active material was changed by the exciting light from the stable condition *A* into the unstable state *B*. Phosphorescence would then result from a gradual breaking down of the unstable compound.[4] Wiedemann pointed out that this hypothesis leads to an exponential law of decay.[5]

While the change called for by the theory here considered has usually been assumed to be of a chemical nature, it was pointed out

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[1] Physical Review, Vol. XXI., p. 257.

[2] E. Wiedemann, Zur Mechanik des Leuchtens. Wied. Ann., Vol. 37, p. 177, 1889.

[3] E. Wiedemann und G. C. Schmidt. Wied. Ann., Vol. 56, p. 177, 1895.

[4] "Das auffallende Licht ruft chemische Modificationen in den phosphorescierenden Körpern hervor, die nachher wieder im umgekehrten Sinne durchlaufen werden und dabei eine Lichtentwickelung hervor rufen. . . . In Bezug auf die chemische Veränderungen dürfte die Anschauung wahrscheinlich sein, dass das Schwefelcalcium etc. in zwei Modificationen, einer stabilen und einer labilen *A* und *B*, bestehen kann. Die Modification *A* wird durch Absorption gewisser Strahlen in die Modification *B* verwandelt, welche allmählich unter Lichtentwickelung sich in *A* zurück verwandelt. . . . Da die Substanzen schon während der Belichtung phosphorescieren, so muss die Rückbildung auch während derselben vor sich gehen." E. Wiedemann, l. c., p. 224–5.

[5] Wiedemann, l. c., p. 226.

by Wiedemann and Schmidt[1] that in many cases there were reasons for looking upon electrolytic dissociation as the more probable cause of luminescence. The increased conductivity of fluorescent solutions during fluorescence[2] adds support to this view. But although it is probable that the exciting light causes a separation of the active molecule into positive and negative parts, it appears to us unlikely that these parts are the ions of ordinary electrolysis. There are many substances like fluorescein and eosin which fluoresce only when dissociated. In such cases fluorescence cannot be due to the recombination of ions; for dissociation and recombination are taking place in an electrolytic solution all the time, and if this were the cause of luminescence we should expect the solution to glow continuously without the action of any exciting light. Fluorescence in such cases must be due to some action of the exciting light upon one of the ions. We have suggested elsewhere that this action may be a dissociation similar to that produced in gases by the Roentgen rays.

Assuming the correctness of the Wiedemann hypothesis in its general features it seems clear that dissociation in the case of photo-luminescence is a result of the violent vibrations set up in the molecules of the active substance by the exciting light. A certain number of the active molecules are actually torn apart, and the resulting negative electrons and positive nuclei exist for a time uninfluenced by their mutual attraction. The vibrations that occur upon the recombination of the ions give rise to luminescence. This view at once explains the well known fact that the light from an isotropic luminescent body is unpolarized, whatever may be the state of polarization of the exciting light.[3]

The fact that the light emitted during luminescence is of different wave-length from the exciting light seems at first to speak against the above explanation of photo-luminescence. Why should the vibrations that occur on recombination differ in period from those originally set up by the exciting light? It is indeed possible that the latter are forced vibrations, whose period bears no simple rela-

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[1] L. c., pp. 244–247.

[2] Nichols & Merritt, PHYSICAL REVIEW, Vol. 19, p. 396, 1904.

[3] Seeming exceptions to this statement probably result from polarization by emission. See Millikan, PHYSICAL REVIEW, Vol. 3, p. 97.

tion to the natural period of the molecule. But it is more reasonable to expect that vibrations which bring about actual disintegration are produced by resonance. If this is true we have to do with the natural period of the molecule in both cases, and it would seem that the light emitted during luminescence should have the same wave-length as the exciting light. In the discussion that follows we venture to make a suggestion which offers an explanation of this difficulty.

In the case of photo-luminescence in solids and liquids the active molecule is always closely surrounded by other molecules. In general these surrounding molecules belong to the solid or liquid solvent in which the active material is dissolved. If we have to deal with the luminescence of a pure substance (if such cases occur), the surrounding molecules are of the same kind as those which participate in the luminescence phenomena. But in either case the period of vibration will be different from what it would be if the vibrating molecules were isolated. Since the change in period will be relatively great for those molecules that are close to their neighbors and smaller for those that are further away, it is seen that the natural period will vary through a considerable range as the active molecules move about, and at each instant there will exist in the substance molecules having all periods lying between certain rather wide limits. The absorption spectrum of the substance therefore consists of bands rather than of lines.[1]

When a molecule is dissociated by the action of the exciting light, the two parts, being electrically charged, will be more strongly attracted by the molecules of the solvent than was the original neutral molecule. Recombination of the separated ions is therefore more likely to occur when the latter are in the immediate neighborhood of the molecules of the solvent, *i. e.*, under conditions which make the period of the resulting vibrations longer, on the whole, than the period natural to the active molecules before dissociation. Since recombination can occur under a variety of conditions a wide range of wave-lengths will be represented in the luminescence spectrum; the latter also will consist of bands rather than of lines.

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[1] Essentially this explanation of the broadening of spectral lines has been discussed in some detail by Galitzin, Wied. Ann. 56, p. 78, 1895.

But on the whole the wave-length of the light emitted during luminescence will be longer than that of the exciting light. The same sort of thing will occur, although in less marked degree, even when the active molecule is itself electrically charged, as in the case of fluorescein. In this case, as well as in that first considered, it may even be that each of the two parts into which the active molecule is dissociated becomes a nucleus to which neutral molecules are attracted so that the ions become heavy aggregations of molecules. This is the assumption usually made regarding the production of ions in gases by the action of Roentgen rays, cathode rays, etc. If this is the real condition of affairs, the reasons for increased wave-length in the light emitted are still more evident.

It will be seen that this way of looking at the phenomena of photo-luminescence gives what might be called a mechanical explanation of Stokes' law. It does not lead us to expect, however, that Stokes' law will always be *exactly* followed. The luminescence spectrum and the absorption spectrum may overlap; in fact, it is to be anticipated that they will do so in the majority of cases. This is in agreement with the more recent experiments on this subject.[1]

Among the other experimental laws of photo-luminescence that are satisfactorily accounted for by the theory of Wiedemann and Schmidt may be mentioned the fact that the form of the luminescence spectrum is the same whatever may be the wave-length of the exciting light.[1] Light corresponding to any part of the absorption band may, if sufficiently intense, produce dissociation. But the manner in which recombination occurs will not depend in any way upon the wave-length of the rays by which the dissociation was produced.

Upon the basis of this theory it is clear also that we should expect no change in the form of the phosphorescence spectrum during decadence. The intensity of phosphorescence will depend at each instant upon the number of recombinations that occur per second, and will therefore diminish as the number of free ions becomes less. But it seems probable that the number of recombinations that occur under such conditions as to give light of a certain wave-length will still remain the same fraction of the whole

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[1] Nichols and Merritt, PHYSICAL REVIEW, Vol. 18, p. 403, 1904.

number. The case has some resemblance to that of the distribution of velocities among the molecules of a gas; if the total number of molecules in a given volume is diminished, the number having a given velocity will also diminish; but this number will still be the same fraction of the whole.

The simplest hypothesis regarding the law of recombination of the ions in a luminescent substance is that which has been applied to the case of ionization in gases.[1] Let the number of positive ions present per c.c. at any time t be n. The number of collisions between a positive and a negative ion will be proportional both to the number of positive ions and to the number of negative ions; and a certain fraction of these collisions will result in recombination. Since positive and negative ions are present in equal numbers we have

$$\frac{dn}{dt} = -an^2,$$

$$\frac{1}{n} = c + at \quad \text{where} \quad c = \frac{1}{n_0}.$$

Since the intensity of phosphorescence is proportional to the number of recombinations per second

$$I = kan^2 = \frac{ka}{(c+at)^2}.$$

This is one form of the expression originally proposed by E. Becquerel to express the decay of long time phosphorescence, and is the same law that was derived on the basis of entirely different theoretical assumptions by H. Becquerel.[2] As was shown in the first part of this paper the equation represents satisfactorily the results of our own experiments with Sidot blende.

In comparing our experimental results with the law just derived it was convenient to write the above expression in a different form: namely

$$\frac{1}{\sqrt{I}} = a + bt$$

where

$$a = \frac{1}{n_0\sqrt{ka}}; \quad b = \sqrt{\frac{a}{k}}.$$

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[1] Rutherford, Philosophical Magazine, Vol. 44, p. 422, 1897.

[2] Comptes Rendus, Vol. 113, p. 618, 1891.

It is to be remembered that if I refers to the intensity at some particular part of the phosphorescence spectrum, k must be regarded as a function of the wave-length.

The fact that the experiments indicate a linear relation between the time and $I^{-\frac{1}{2}}$ has already been pointed out, and reference to the tables on pages 284–5 shows that the differences between the computed and observed values of t, which are usually small, are entirely unsystematic. It is possible to test the law still further by considering the values of the constants a and b. Except in the case of the last curve of Table I., the data refer to curves of decay for different wave-lengths, but with the same excitation. a and n_0 are therefore constant, while k depends upon the wave-lengths. It will be noticed that

$$\frac{a}{b}=\frac{1}{n_0\sqrt{ka}}\cdot\sqrt{\frac{k}{a}}=\frac{1}{n_0 a}.$$

This quotient should therefore be a constant for all curves taken with the same excitation and under similar experimental conditions. The values of the ratio a/b for the three curves of Table III. show considerable variation from equality, being 1.5, 2.0, and 1.7. The values of the ratio for the first three curves of Table I. are 1.73, 1.75 and 1.65. In view of the difficulty of maintaining constant conditions in the experiments on phosphoresence the agreement between these three values is highly satisfactory. As already stated the observations at 0.483 μ in Table II., probably on account of some experimental error, cannot be represented by the expression here considered, so that the value of a/b for this curve cannot be determined. But for the curves taken at 0.512 μ and 0.547 μ (Table II.) the quotient a/b has the values 2.32 and 2.43, respectively. Here, too, the agreement is all that could be expected.[1] Our results therefore afford strong confirmation not only of the conclusion reached in our last communication that all parts of the green band decay at the same rate, but also of the general theory of phosphorescence that we have used in deriving the law of decay.

The data permit still another test of the general theory, the result

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[1] There is no reason why the values a/b for Table I. should be the same as those for Table II. or III. since the observations were made several weeks apart, and with no attempt to keep the intensity of the comparison source the same in the different cases.

of which is less satisfactory. It will be remembered that in the case of the fourth curve of Table I. the exciting light was less intense than that used with the other curve for 0.512 μ. The observations for the fourth curve were made on the same day as those for the second curve, and although the former were made in the afternoon and the latter in the forenoon, every attempt was made to keep the comparison source the same in the two cases and to have all the other experimental conditions as nearly as possible constant. If we compare the two curves for 0.512 μ in Table I., we see that a and k have the same value for both, while n_0 is different. The constant b, however, is independent of n_0. This constant should therefore have the same value for both curves; in other words the straight lines obtained by plotting $I^{-\frac{1}{2}}$ should be parallel. As a matter of fact the values of b determined for the two curves are 0.045, for the second curve of Table I., and 0.052 for the fourth. The fact that the two values are unequal is shown in Fig. 37 by the lack of parallelism of the two lines A' and B'.

The law of decay derived upon the basis of the simple considerations outlined above, while representing the results of observation during the early stages of phosphorescence with surprising accuracy, can not be regarded as more than a first approximation to the correct expression. When the curve of decay is followed for several minutes instead of for several seconds a systematic variation is found from the linear relation between $I^{-\frac{1}{2}}$ and t. Experiments dealing with the long-time phosphorescence of Sidot blende and certain other substances will be described in our next paper.