STUDIES IN LUMINESCENCE.

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

X. THE PHENOMENA OF PHOSPHORESCENCE CONSIDERED FROM THE STANDPOINT OF THE DISSOCIATION THEORY.[1]

BY ERNEST MERRITT.

IN an important paper on luminescence published in 1895 Wiedemann and Schmidt[2] have suggested that in many instances, notably in the case of solid solutions, the effect of light, or of other exciting agents, is to produce electrolytic dissociation of the dissolved active substance, and that the light emitted during luminescence is to be explained as the result of the molecular vibrations which occur either during the process of dissociation or when the ions recombine. Wiedemann and Schmidt discussed the various types of luminescence in considerable detail and showed that the theory proposed by them will account for the phenomena, at least qualitatively, in a very satisfactory way.

In one of the previous papers of this series it was pointed out that this theory leads to a simple explanation of Stokes' Law,[3] which has usually proved a stumbling block in the development of theories of luminescence; and some progress was also made toward the development of a quantitative theory of phosphorescence on the basis of the dissociation hypothesis.

In view of what has already been accomplished by the theory of Wiedemann and Schmidt it appears to the writer that this theory is by far the most promising of those that have yet been proposed. In discussing the theoretical significance of the observations on phosphoresence described in the preceding papers of this series, it has therefore seemed advisable to use this theory as a basis.

The present paper is devoted chiefly to a discussion of the theory of phosphorescence. No attempt will be made to develop a complete theory. It is intended rather to consider in turn the various

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[1] The ninth paper of this series, whose publication has been unavoidably delayed, will appear in the near future.

[2] Ann. der Phys., Vol. 56, p. 177, 1895.

[3] Nichols and Merritt, PHYS. REV., Vol. 22, p. 279, 1906.

factors which may have an influence on the phenomena, and to determine so far as possible the nature of this influence. Comparison with experimental results will then make it possible to form an opinion of the relative importance of the various factors considered.

It will facilitate the discussion if we consider first the requirements which a satisfactory theory must meet. The most important experimental results in the case of photoluminescence are briefly mentioned below.

SUMMARY OF EXPERIMENTAL LAWS.

1. Stokes' Law.

2. If we isolate a single band of the luminescence spectrum it is found that the distribution of intensity throughout the band is independent of the intensity and wave-length of the exciting light.[1]

3. The light emitted during the luminescence of an isotropic substance is unpolarized, whatever may be the condition of polarization of the exciting light.

4. During the decay of phosphorescence each band of the luminescence spectrum behaves as a unit; *i. e.*, the wave-length of maximum intensity and the relative distribution of intensity throughout the band remain unchanged.[2]

The theoretical aspect of these general laws was discussed in the sixth paper of this series,[3] and it was then pointed out that the laws are directly deducible from the dissociation theory.

To these four general laws must be added the following experimental facts connected with the decay of phosphoresence:[4]

5. *Form of Decay Curve.* — The curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of t as abscissas is a straight line for small values of t; it changes to a curve concave towards the axis of t as t increases; but for still larger values of t the relation between $I^{-\frac{1}{2}}$ and t is again linear, and remains so until I becomes too small to measure. In other words the decay curve is dependent on the intensity and duration of ex-

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[1] This law, first enunciated by Lommel, is discussed in the second and third articles of this series. See PHYS. REV., Vol. 18, p. 403, and Vol. 19, p. 18.

[2] Nichols and Merritt, PHYS. REV., Vol. 21, p. 247.

[3] PHYS. REV., Vol 22, p. 279.

[4] Nichols and Merritt, PHYS. REV., Vol. 22, p. 279; Vol. 23, p. 37; Vol. 25, p. 362.

citation. The slant is altered in each of the straight parts by a change in either of these two factors in the excitation.

6. *Hysteresis.* — The behavior of a phosphorescent substance with a given excitation depends upon its previous history. Some semi-permanent change is produced by excitation which persists for several hours, or even for several days, after visible phosphorescence has ceased.

7. *Effect of Red and Infra-red Rays.* — In the case of certain substances the semi-permanent condition produced by excitation may be destroyed and the material restored to a standard state by a brief exposure to the red and infra-red rays. The effect of the longer waves[1] during phosphorescence is to accelerate the decay. In some substances, but not in Sidot blende, the first effect is to increase the brightness of phosphorescence, this temporary effect being followed by decay more rapid than the normal.

Becquerel's Explanation of the Form of the Decay Curve.

In the case of a homogeneous substance free from any disturbances due to absorption and diffusion it is readily shown that the decay of phosphorescence, as predicted by the dissociation theory, should follow the law[2]

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

where I is the intensity of phosphorescence at any time t after the end of excitation. This law, first proposed as an empirical relation by E. Becquerel, has also been derived by H. Becquerel on the basis of an entirely different theory.[3]

The decay of phosphorescence in gases appears to be strictly in accordance with this law.[4] Under certain special conditions as regards temperature, etc., the law is very closely obeyed by zinc sulphide[5] and even by Balmain's paint.[6] But in the great majority of

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[1] Although the rays that produce these effects are generally of longer wave-length than the rays that excite luminescence, this is not always the case. Several exceptions are cited by Dahms.

[2] Nichols and Merritt, PHYS. REV., Vol. 22, p. 279, 1906.

[3] H. Becquerel, Compt. Rend., Vol. 113, p. 618, 1891.

[4] C. C. Trowbridge, PHYS. REV., Vol. 26, p. 515, 1908.

[5] C. A. Pierce, PHYS. REV., Vol. 26, p. 312, 1908.

[6] C. A. Pierce, PHYS. REV., Vol. 26, p. 454, 1908.

instances the phosphorescence of solids decays in accordance with a more complicated law. As stated above the curve obtained by plotting values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of t as abscissas is not linear throughout, as the simple theory would lead us to expect. The curve is straight both for small values of t and for large values of t, but shows a sharp curvature for intermediate values.

It has been suggested by H. Becquerel that this form of curve is to be accounted for by assuming that the phosphorescence spectrum consists of two bands, each of which obeys the simple law, but having different rates of decay. If a decay curve is plotted for each of the two assumed bands the equations of the two curves will be

$$I_1^{-\frac{1}{2}} = a_1 + b_1 t \quad \text{and} \quad I_2^{-\frac{1}{2}} = a_2 + b_2 t$$

and each of the two curves will be a straight line. But if we plot $I^{-\frac{1}{2}}$ against t, where I is the observed *total* intensity $(I = I_1 + I_2)$

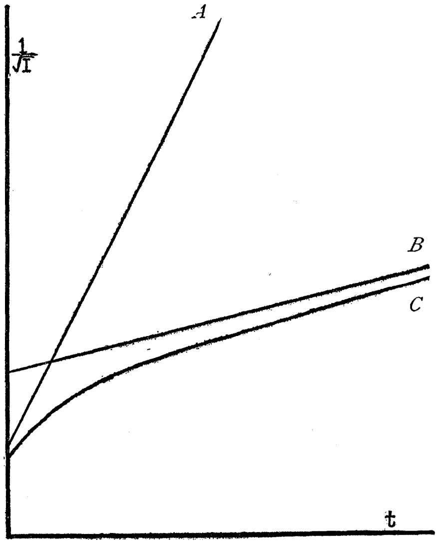

Fig. 69. Illustrating Becquerel's explanation of the form of the decay curve in solids.

the resulting curve will not be straight but will take the form shown by curve C, Fig. 69. In this figure curves A and B are the decay curves for the two bands taken separately. In the case represented in the figure the two bands are assumed to decay at widely different rates, and the band which decays more rapidly (A) has initially the greater intensity. It will be seen that under these circumstances the decay curve for total intensity has all the characteristics of the curves determined by experiment. Becquerel cites one substance for which the observed intensity can be represented by the expression

$$I = \frac{1}{(a_1 + b_1 t)^2} + \frac{1}{(a_2 + b_2 t)^2}$$

with remarkable accuracy. In the case of this particular substance Becquerel also found independent evidence of the existence of two bands in the phosphorescence spectrum.

This way of accounting for the form of the decay curve was also proposed by Pierce in discussing the decay of phosphorescence in Emanationspulver, and has been shown by him to give a very satisfactory explanation of the change in the form of the decay curve resulting from changes in temperature.

In the case of our own observations on Sidot blende we have expressed the opinion that the curves obtained are to be regarded as showing the decay of the green band alone; for although Sidot blende also possesses bands in the blue and violet, these decay so quickly and are of such small luminosity that they can scarcely affect the curves to any appreciable extent. In the more recent work of Werner[1] special precautions were taken in the choice of a substance and in the use of color screens to make certain that one band only was studied; yet the curves obtained are of exactly the same type as those found by other observers.

The work of Werner, even more strongly perhaps than our own work with Sidot blende, thus appears to discredit any explanation of the form of the decay curve that is based upon the assumption of two bands in the phosphorescence spectrum. It cannot be denied, however, that two bands may well be present even when special precautions of this kind are taken, and even when the spectrophotometer shows no indication of a double band. The bands of a phosphorescence spectrum are ordinarily so broad that two bands lying close together might readily appear as one. If the

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[1] A. Werner, Ann. der Phys., Vol. 24, p. 164, 1907.

case is one where the bands actually overlap it would be impossible to make observations on one alone without working at the extreme edge of the double band, where the intensity would probably be too small to permit of accurate observations. I am at present unable to see any method of directly testing the matter. Since the assumption of two nearly coincident bands offers so direct an explanation of the form of the decay curve, and since it seems certain that curves may be plotted on the basis of this assumption which deviate from the observed curves by less than the experimental errors, it must be admitted that the hypothesis has much in its favor.

There are several reasons, however, for looking upon this explanation of the form of the curve with suspicion. In the first place it does not account either for the remarkable changes produced in the decay curves by varying the intensity and duration of excitation, or for the phenomena of hysteresis that have been observed in almost all cases of long time phosphorescence. It also leaves untouched the question of the effects produced by exposure to the longer waves. An even more serious objection is the fact that it is necessary to assume the existence of two nearly coincident bands in *all* cases of long time phosphorescence; for upon replotting the decay curves obtained by different observers with $I^{-\frac{1}{2}}$ and t as coördinates it is found that the curves are of the same type for all substances that have thus far been tested. It is hardly credible that this is accidental. Only two explanations appear to me to be possible: either the existence of two nearly coincident bands is an essential characteristic of substances showing long time phosphorescence, or else the peculiarities exhibited in the form of the decay curve are to be explained in some manner which does not involve the assumption of two bands at all. While it may prove of interest at some later time to develop the theory along the lines suggested by the first of these alternatives, the present discussion will be based upon the acceptance of the second, and I shall consider in what ways the form of the decay curve, as well as certain other peculiarities of phosphorescence, may be explained in substances possessing only one band in the phosphorescence spectrum.

ABSORPTION EFFECTS.

If a homogeneous substance possessing only one band in its phosphorescence spectrum is uniformly excited throughout, and if the light emitted by the interior portions suffers no diminution by absorption before reaching the surface, then according to the dissociation theory here considered the decay of phosphorescence will be in accordance with the law

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

These conditions, however, can never be exactly attained. The exciting light must be absorbed to some extent, for otherwise no energy would be available to produce phosphorescence. The excitation will therefore be greatest at the surface, and will diminish, at a rate determined by the absorbing power of the material, as we pass to points within. Since the ions are in consequence more numerous in the surface layers, and since the number of recombinations per second, which determines the intensity of phosphorescence, is proportional to the square of the number of ions, it is clear that the light emitted during the early stages of decay will come chiefly from the surface. As decay proceeds, however, the relatively high rate of recombination at points where n is large will cause a rapid approach to uniformity of ionic concentration, and the part contributed to the total light by the interior of the mass will become increasingly important. At first the intensity of phosphorescence is approximately proportional to V_1an^2, where V_1 is the volume of the surface layer that is chiefly effective. Later, when the light from the interior becomes comparable in intensity with that from the surface, the phosphorescence will be approximately proportional to V_2an^2, where $V_2 > V_1$. In terms of the total number of ions, N, the two intensities will thus be approximately proportional to $a/V_1 \cdot N^2$ and $a/V_2 \cdot N^2$. So far as the slant of the decay curve is concerned this is equivalent to a decrease in the coefficient of recombination and will result in making the curve concave toward the axis of t. Absorption of the emitted light will complicate the phenomena but will not modify the general result. The effect of absorption is therefore to produce a change in the form of the decay curve which is at least in the right direction to account for the observed deviation from linearity.

In discussing the effect of absorption in detail I shall assume that both the exciting light and the emitted light suffer absorption, the two coefficients of absorption being β and γ respectively. At any depth x below the surface the intensity of the exciting light will be

$$E = E_0 e^{-\beta x}.$$

Assuming that ions are produced at a rate proportional to E and that excitation has proceeded for a sufficient time to produce a steady condition, the number of ions per cubic centimeter at any depth x will be determined by the equation

$$\frac{dn}{dt} = 0 = hE - \alpha n_0^2 = hE_0 e^{-\beta x} - \alpha n_0^2,$$

$$n_0 = \sqrt{\frac{hE_0}{\alpha}}\, e^{-\frac{1}{2}\beta x}.$$

If n is the number of ions per cubic centimeter at the time t we have

$$n = \frac{1}{1/n_0 + \alpha t}.$$

and the light emitted per unit volume, denoted by i, is

$$i = p\alpha n^2 = \frac{p\alpha}{(1/n_0 + \alpha t)^2},$$

p being the light emitted as the result of one recombination.

Since the emitted light suffers absorption the amount contributed to the total observed intensity by a layer of thickness dx will be

$$i\,dx\,e^{-\gamma x} = \frac{p\alpha e^{-\gamma x} dx}{(1/n_0 + \alpha t)^2}$$

and the total intensity is

$$I = p\alpha \int_0^\infty \frac{e^{-\gamma x} dx}{(ae^{\frac{1}{2}\beta x} + \alpha t)^2} = p\alpha \int_0^\infty \frac{e^{-\gamma x} e^{-\beta x} dx}{(a + \alpha t e^{-\frac{1}{2}\beta x})^2},$$

where

$$a = \sqrt{\frac{\alpha}{hE_0}}.$$

Putting

$$ate^{-\beta x/2} = z$$

so that

$$dz = -\frac{a\beta t}{2}e^{-\frac{\beta x}{2}}dx \quad \text{and} \quad e^{-\gamma x} = \left(\frac{z}{at}\right)^{\frac{2\gamma}{\beta}},$$

$$I = -\frac{2pa}{\beta(at)^{m+2}}\int_{at}^{0}\frac{z^{m+1}dz}{(a+z)^2},$$

where $m = 2\gamma/\beta$.

Successive partial integration gives

$$I = -\frac{2pa}{\beta(at)^{m+2}}\left[\frac{1}{m+2}\frac{z^{m+2}}{(a+z)^2} + \frac{2}{\overline{m+2}\cdot\overline{m+3}}\frac{z^{m+3}}{(a+z)^3} + \frac{2\cdot 3}{\overline{m+2}\cdot\overline{m+3}\cdot\overline{m+4}}\frac{z^{m+4}}{(a+z)^4} + \cdots\right]_{at}^{0}.$$

Upon putting in the limits this becomes

$$I = \frac{2pa}{(m+2)\beta}\cdot\frac{1}{(a+at)^2}\left[1 + \frac{2}{m+3}\cdot\frac{at}{a+at} + \frac{2\cdot 3}{\overline{m+3}\cdot\overline{m+4}}\left(\frac{at}{a+at}\right)^2 + \cdots\right].$$

The series in the brackets has the value 1 for $t = 0$ and as t becomes large approaches the series

$$1 + \frac{2}{m+3} + \frac{2\cdot 3}{\overline{m+3}\,\overline{m+4}} + \cdots = S.$$

If the decay curve is plotted in the usual way with $I^{-\frac{1}{2}}$ and t as coördinates it is clear that the change in slant in passing from small values of t to large values will depend upon S and will be greatest when S is greatest. The maximum deviation from linearity in the form of the decay curve which can result from absorption will therefore be produced when $m = 0$, *i. e.*, when $\gamma = 0$. To determine whether absorption is sufficient to account for the observed type of curve I shall therefore consider first this special case for which the effect is greatest.

For $m = 0$ we have

$$I = -\frac{2pa}{\beta(at)^2}\int_{at}^{0}\frac{zdz}{(a+z)^2} = -\frac{2pa}{\beta(at)^2}\left[-\frac{z}{a+z} + \log(a+z)\right]_{at}^{0}.$$

Putting in the limits this becomes

$$I = \frac{2p\alpha}{\beta(\alpha t)^2}\left[\log\left(1 + \frac{\alpha t}{a}\right) - \frac{\frac{\alpha t}{a}}{1 + \frac{\alpha t}{a}}\right].$$

Writing θ for $\alpha t/a$

$$I = \frac{2p\alpha}{a^2\beta}\cdot\frac{1}{\theta^2}\left[\log(1+\theta) - \frac{\theta}{1+\theta}\right].$$

The curve for θ and $I^{-\frac{1}{2}}$, computed in accordance with this equation, is plotted in Fig. 70, the quantity $2p\alpha/a^2\beta$ being put equal to unity. This curve may be looked upon as showing the relation between $I^{-\frac{1}{2}}$ and t for $\alpha/a = 1$. The curve for any different value of α/a may then be found by changing the vertical and horizontal scales to correspond to the change in α/a.

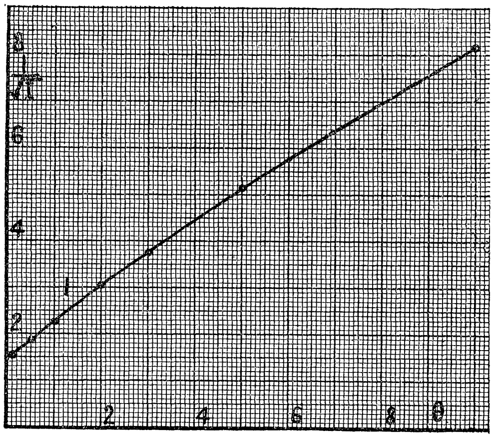

Fig. 70. Showing the greatest deviation from linearity in the decay curve which can be produced by absorption alone.

The curve of Fig. 70 is similar in form to the decay curves observed in the case of short excitation. Pierce[1] has also observed curves of nearly this form with zinc sulphide. It is possible, there-

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[1] C. A. Pierce, PHYS. REV., Vol. 26, p. 314, Fig. 1. In our own work with this same substance, "Emanationspulver," we found a decay curve of the usual type, *i. e.*, with a well marked "shoulder" at $t = 20$ sec. (PHYS. REV., Vol. 28, p. 50, Fig. 51). It is interesting to inquire whether the difference is due to the repeated heating and cooling to which Pierce's material was subjected.

fore, that the relatively slight deviation from linearity in such cases is to be ascribed to absorption. But in the case of the majority of decay curves it is clear that absorption is not to be regarded as an important factor; for no change of scale can bring about any close resemblance between the curve of Fig. 70 and the decay curves usually observed for long and moderately long excitation.

Influence of Irregularities in the Distribution of the Active Material.

Luminescent substances are in most cases solid solutions. In fact it is doubtful whether luminescence can occur in an absolutely pure substance. Pure calcium sulphide for example is not phosphorescent; but the addition of a small amount of some other metal, such as manganese or copper, gives it the power to phosphoresce brilliantly. The method of preparating the phosphorescent sulphides is such as to bring about a very intimate mixture of the constituents, and it is natural to think of the manganese, copper, or other active material as being dissolved in the sulphide.

So little is known regarding the nature of solid solutions that we cannot say with certainty whether such substances are to be regarded as strictly homogeneous or not. Especially in the case of crystals it seems not improbable that the molecules of the solute may not be uniformly distributed throughout the mass of the solvent, but may to a greater or less extent collect in groups or minute crystals. Any lack of uniformity in the distribution of the active substance will cause a corresponding variation in the concentration of the ions produced by the exciting light; and if the nature of the solvent is such as to permit of diffusion the phenomena will be complicated by the fact that a redistribution of the ions will occur during excitation and decay. Even without diffusion, however, the form of the decay curve will be modified. For since the rate of recombination is proportional to the square of the ionic concentration the intensity of phosphorescence will decay at different rates in different parts of the mass. The effect on the decay curve will be similar to that produced by absorption; in fact the decay curve is modified by absorption of the exciting light only because of the resulting lack of uniformity in the ionic concentration at different depths below the surface.

Our complete ignorance of the distribution of the active material makes it almost useless to attempt any exact treatment of the problem. It is possible, however, without questionable assumptions or great analytical complexity to predict the general character of the effect to be expected.

Let n be the number of ions per unit mass at any point; n is then some unknown function of the position of the point in question and of the time that has elapsed since the decay began. The number of recombinations per second will be an^2 per unit volume, and the number of recombinations for the whole mass will be $\int an^2 d\tau$, where $d\tau$ is an element of volume. Disregarding the absorption of the emitted light we have

$$I = k\alpha \int n^2 d\tau.$$

Since ions are destroyed only by recombination

$$\frac{dN}{dt} = -a \int n^2 d\tau$$

where N is the total number of ions.

If $\bar{n}$ is the volume average of n, and $\overline{n^2}$ the volume average of n^2, so that

$$\bar{n} = \frac{1}{\tau}\int n\, d\tau = \frac{N}{\tau}, \quad \overline{n^2} = \frac{1}{\tau}\int n^2 d\tau, \quad \frac{dN}{dt} = -\alpha\tau\overline{n^2}.$$

If we put

$$\rho = \frac{\overline{n^2}}{(\bar{n})^2}, \quad \overline{n^2} = \rho(\bar{n})^2 = \rho\frac{N^2}{\tau^2} \quad \text{and} \quad \frac{dN}{dt} = -\alpha\tau\rho\frac{N^2}{\tau^2} = -\frac{\alpha\rho}{\tau}N^2,$$

$$\frac{1}{N} - \frac{1}{N_0} = \frac{a}{\tau}\int_0^t \rho\, dt.$$

Writing ρ_1 for the average value of ρ between o and t

$$N = \frac{1}{\frac{1}{N_0} + \frac{\alpha\rho_1}{\tau}t}, \quad I = -k\frac{dN}{dt} = \frac{k\alpha}{\tau}\cdot\frac{\frac{d}{dt}(\rho_1 t)}{\left(\frac{1}{N_0} + \frac{\alpha\rho_1}{\tau}t\right)^2}.$$

Since

$$\rho_1 = \frac{1}{t}\int_0^t \rho\, dt, \qquad \frac{d}{dt}(\rho_1 t) = \rho$$

$$\therefore \frac{1}{\sqrt{I}} = \sqrt{\frac{\tau}{k\alpha\rho}}\left(\frac{1}{N_0} + \frac{\alpha\rho_1}{\tau}t\right).$$

Although we are unable to determine ρ and ρ_1 as functions of t it is clear that both will decrease as t increases. It is clear also that the change will become less rapid as the decay proceeds, and that both ρ and ρ_1 will sooner or latter become nearly constant. When $I^{-\frac{1}{2}}$ is plotted against t we shall therefore obtain a curve which is concave downward and which finally becomes a straight line. In other words the decay curve will agree in form with the curves determined by experiment.

The effect upon the decay curve of an irregular distribution of the active substance may be illustrated by the following simple case. Let the active material be uniformly distributed except that small regions occasionally occur where the concentration is abnormally large. The whole volume may thus be divided into two parts, v_1 and v_2. The distribution of the active material is uniform throughout each part, but the concentration in v_1 is different from that in v_2. When the substance is excited to phosphorescence the ionic concentration will also differ in the two regions. Let the number of ions per cubic centimeter at the end of excitation be n_1 in the volume v_1 and n_2 in the volume v_2. Throughout the region v_1 the intensity of the light emitted per cubic centimeter will be

$$i = \frac{\alpha k}{(1/n_1 + \alpha t)^2}$$

and the *total* intensity at any instant due to this part of the whole mass will be

$$I_1 = \frac{\alpha k v_1}{(1/n_1 + \alpha t)^2}.$$

The light emitted by the volume v_2 is given by the similar expression

$$I_2 = \frac{\alpha k v_2}{(1/n_2 + \alpha t)^2}$$

and the total intensity is

$$I = I_1 + I_2 = ak\left(\frac{1}{(a_1 + b_1 t)^2} + \frac{1}{(a_2 + b_2 t)^2}\right)$$

where

$$a_1 = \frac{1}{n_1\sqrt{v_1}}, \quad a_2 = \frac{1}{n_2\sqrt{v_2}},$$

$$b_1 = \frac{a}{\sqrt{v_1}}, \quad b_2 = \frac{a}{\sqrt{v_2}}.$$

It thus appears that the form of the decay curve is the same as though the substance possessed two bands, coincident as regards wave-length, but differing in rate of decay.

It is not at all unlikely that a condition approaching that assumed in this illustrative case actually exists in most phosphorescent substances. Upon considering the method used in preparing the phosphorescent sulphides, for example, it seems probable that the distribution of the active substance will be far from uniform. When the mixture is first prepared, and before calcination, the active material is unquestionably in the form of small discrete masses distributed irregularly through the mixture. Upon heating to redness diffusion will occur to a greater or less extent, depending upon the temperature and the duration of heating. But even at high temperatures this will be a slow process, and considerable variations in concentration are likely to remain even after prolonged heating. It is to be expected, therefore, that the phosphorescent sulphides will contain numerous nuclei of high concentration surrounded in each case by a region where the concentration is relatively small.[1]

After calcination it is often noticed also that the phosphorescence is very far from being uniform throughout the mass. Owing probably to accidental differences in concentration, or to differences in the heat treatment, the phosphorescence often differs greatly in intensity and even in color in different parts of the same mass. A phosphorescent powder made from such a mass, while presenting the appearance of homogeneity to the unaided eye, would differ

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[1] Since a more complete diffusion of the active material will result from prolonged heating it is to be expected, other conditions being the same, that the duration of phosphorescence will be prolonged by increasing the time of heating. This agrees with the facts observed in the preparation of the phosphorescent sulphides.

greatly from point to point in the concentration of the active material.[1] Even if the mixture were so perfect that the microscope could detect no irregularities a wide deviation from linearity in the decay curve is to be expected. It is a significant fact that with one exception all decay curves thus far recorded have been determined with powders prepared in practically the same way that the phosphorescent sulphides are prepared. In fact most of the substances tested were sulphides. The exception noted above was natural willemite[2] in which case the variation in brightness over the surface tested was plainly visible.

It thus appears that irregularities in the distirbution of the active substance are sufficient to explain the deviation from linearity in all the decay curves thus far observed. Such irregularities of distribution are not merely probable, but in many cases are perfectly obvious. But while the distribution of the active material is probably in all cases an important factor, it cannot be the only factor of importance. With Balmain's paint, Pierce has found that the decay curve, which possesses the usual shoulder at ordinary temperatures, becomes almost exactly linear at a temperature of 74°,[3] while for higher temperatures it again shows a curvature of the usual kind. It appears highly improbable that such changes are brought about by temporary changes in the distribution of the active substance. Non-uniformity in the distribution of the active material also offers no explanation of the phenomena of hysteresis or of the effect of the infra-red rays.

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[1] While we are chiefly concerned at present with the influence of lack of homogeneity upon the decay curve, it can scarcely be doubted that the effect upon the phosphorescence spectrum is fully as important. For some reason different parts of the mass are differently affected by the process of calcination. This may be due to differences in concentration throughout the mass, or to the fact that the effect of the surrounding gas varies from point to point. When such a mass is powdered and mixed the effect is the same as though we were to make an intimate mixture of several entirely different phosphorescent substances. Each constituent has its own band or group of bands, characterized by definite wavelengths and periods of decay, which differ according to the conditions of preparation. It is not surprising that the phosphorescence spectrum of such a material is complex ; and we can scarcely expect simple laws to apply to any of the phenomena exhibited by such a mixture.

[2] The decay of phosphorescence in a speciman of willemite possessing a long time phosphorescence has been studied by Nichols and Merritt, PHYS. REV., Vol. 23, p. 52, Fig. 53. Willemite whose phosphorescence dies out with great rapidity has been studied by Waggoner, PHYS. REV., Vol. 27, p. 209.

[3] PHYS. REV., Vol. 26, p. 458, Fig. 26.

Diffusion Effects

Whenever irregularities exist in the distribution of the active substance there will be a tendency for diffusion to occur. Under ordinary conditions this tendency is probably neutralized by forces which act to keep the distribution unaltered, so that so long as the substance remains in the molecular form the condition is to be regarded as a stable one for the temperature and pressure at which the phosphorescent substance normally exists.

But when the material is excited to luminescence a part of the active substance will be dissociated, and since the resulting ions will possess a different mobility and will be acted upon by different forces from those that determine the behavior of the original neutral molecules, the condition of equilibrium will be destroyed, and some change in the distribution of the active substance is to be expected.

An exact discussion of the effects of diffusion would present great difficulties; for the fact that diffusion and recombination occur at the same time greatly complicates the analytical treatment. It is probable also that in crystals the diffusion constant will be different for different directions. It is clear, however, that the influence of diffusion upon the form of the decay curve must be similar to that produced by an irregular distribution of ions without diffusion. In fact the discussion of the preceding section applies without modification to the case of substances in which diffusion of the ions may occur. Diffusion, however, will increase the rapidity with which uniformity of ionic concentration is approached during decay; and since diffusion will be most active when large concentration gradients exist, the effects of diffusion will be greatest in the early stages of decay. In cases where diffusion is an important factor we should therefore expect a sharper curvature in the early part of the curve, and a more rapid approach to linearity, than in cases where diffusion is absent.

It is not impossible that diffusion is sometimes important even when there is practically complete uniformity in the distribution of the active substance. Owing to the absorption of the exciting light the ionization produced in the surface layer will be more intense than that produced at points beneath the surface. If the absorption is large a large gradient may thus be produced in the ionic concentration, and diffusion from the surface layers inward will bring about a change in the decay curve similar in character to that caused by irregularities in the distribution of the active substance. Diffusion produced in this way would ultimately result in an appreciable diminution in the surface concentration of the active material, and we should therefore expect that the intensity of luminescence would be diminished in such a substance by prolonged excitatation. No effect of this kind has been observed by us in the case of Sidot blende, but the observations of Werner[1] with a SrZn compound show evidence of fatigue resulting from prolonged excitation.

The change in the form of the decay curve due to changes in the duration of excitation may be explained, at least in a general way, as a result of diffusion. Diffusion of the ions will occur during excitation as well as during decay. After prolonged excitation, therefore, the volume occupied by ions will be greater than after short excitation, and the rate of decay — in other words the slant of the decay curve — will be correspondingly reduced.[2]

Diffusion also offers an explanation of the phenomena of hysteresis in phosphorescence substances. After prolonged excitation and subsequent decay the neutral molecules that result from recombination will be distributed through a larger volume than before. Since the original distribution of the active material was a stable one there will be a gradual return to the normal distribution. But this will be a slow process and may well require several days for its completion. In the mean time the material is in such a condition that the decay following renewed excitation will be more gradual than the normal, even for a short excitation. The spreading out of the active substance by diffusion, which would normally require a long excitation, has already been accomplished by the preceding excitation, whose effects have not yet disappeared. Hys-

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[1] Werner, A., Ann. der Phys., Vol. 24, p. 164, 1907.

[2] If the volume occupied by ions is v_1 for short excitation and v_2 for long excitation, the ionic concentrations will be n/v_1 and n/v_2 respectively and the two intensities of phosphorescence will be proportional, an^2/v_1 and an^2/v_2. Prolonged excitation therefore produces an effect which is equivalent to a diminution in the coefficient of recombination.

teresis effects such as those exhibited in Fig. 40[1] are therefore to be expected.

If this explanation of hysteresis is correct the effect of the infra-red rays must be to facilitate the return of the substance to its normal condition: in other words to increase the rapidity of the diffusion by which the original distribution of the active material is restored. It is natural to expect such an effect in substances which are able to absorb the infra-red rays. But if the restoration is accomplished by the diffusion of neutral ions the rapidity of the action is surprising, for with strong infra-red rays we have found that an exposure of only a few seconds is sufficient to restore Sidot blende to its standard condition.[2]

INFLUENCE OF IONIC GROUPING.

In discussing thermo-luminescence and the effect of infra-red rays upon phosphorescence Wiedemann and Schmidt[3] have suggested that some of the ions produced during excitation form semi-stable combinations or groups with the neutral molecules of the solvent, and that these groups may afterwards be broken down, and the ions liberated, by rise in temperature or by the absorption of infra-red rays. The formation of such groups as the result of ionization seems extremely probable, especially in the case of solids, and can scarcely fail to be of importance in any satifactory theory of phosphorescence. Introducing such additional hypotheses as are necessary to give definiteness to the suggestion of Wiedemann and Schmidt let us consider what the influence of such ionic groups will probably be.

We shall assume that the first effect of the exciting light is to produce dissociation in a part of the active material. The dissociation assumed may be either chemical or electrolytic;[4] and if of the

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[1] PHYS. REV., Vol. 23, p. 41, 1906.

[2] Nichols and Merritt, PHYS. REV., Vol. 25, p. 362, 1906.

[3] Ann. der Phys., Vol. 56, p. 247, 1895.

[4] Since the electro-magnetic disturbance that constitutes light can get a hold on the molecules of the active material only by exerting forces upon the electrical charges in the molecule, and will always tend to separate the positive and negative parts, it appears probable that the first effect of the exciting light is always to produce some type of electrolytic dissociation, and that any chemical changes which may be exhibited are secondary effects.

latter type it may be either similar to the dissociation of ordinary electrolysis, or may consist of the expulsion from the molecule of one or more electrons, and thus resemble more closely the ionization of a gas by X-rays. For the sake of definiteness we shall assume that the effect of the exciting light is to produce such violent vibrations as to liberate a single electron from the molecule.

The two ions produced in this type of dissociation will differ greatly in mobility. The negative ion, owing to its small mass, will possess a velocity hundreds of times greater than that of the heavy positive ion, and in consequence will move about in the substance with considerable freedom. While the electrons will at times attach themselves to the molecules of the solid solvent this condition will usually be only temporary. We may assume in general that a constant fraction of the whole number of negative ions consists of electrons that are moving freely. The positive ions on the other hand will possess only a small mobility. While some of these ions will remain free, it is to be expected that many will attach themselves to molecules of the solvent or to undissociated molecules of the active substance. It is to be noted that the small velocity of the positive ions makes it probable that the groups formed by the union of a positive ion with a neutral molecule will be far more permanent than similar groups formed by the negative ion.

It will be seen that the collisions between positive and negative ions, which lead to the more or less gradual decay of the ionized condition after the exciting light has ceased to act, will be of three different kinds: (1) collisions between a negative ion and a free positive ion; (2) collisions between a negative ion and a positive ion that has attached itself to a neutral molecule of the solvent, and (3) collisions between a negative ion and a positive ion that is attached to a neutral molecule of the active substance. The number of modes of recombination may in fact be greater than three, since the positive ion may become the nucleus of more complicated molecular groups. We shall, however, restrict the discussion to cases in which there are only three modes of recombination.

When recombination occurs it is to be expected that vibrations will be set up in the resulting neutral molecule, and these vibrations, in the theory here considered, are assumed to be the source of the light emitted during the phosphorescence. But the vibrations corresponding to the different modes of recombination will probably differ in violence, in frequency, and in radiating power.

Of the total number n of positive ions at any time t let φn be free, and ψn attached to neutral molecules of the active substance; then $(1 - \varphi - \psi)n$ will be attached to molecules of the solvent. φ and ψ are proper fractions whose sum is less than unity, and which, in general, are functions of t, for the distribution of the positive ions will be subject to alteration during the decay of phosphorescence as well as during excitation. The number of recombinations between a free positive ion and an electron in unit time will be proportional to the number of free positive ions φn, and to the number of free negative ions n, and may therefore be put equal $\alpha_1\varphi n^2$, where α_1 is the coefficient of recombination. If the energy radiated as light due to one recombination is p_1 the intensity of the phosphorescence due to this mode of recombination will be

$$I_1 = p_1\alpha_1\varphi n^2.$$

Similarly

$$I_2 = p_2\alpha_2\psi n^2,$$

$$I_3 = p_3\alpha_3(1 - \varphi - \psi)n^2,$$

for the other two types of recombination.

The total phosphorescent light will thus consist of three parts. If the different modes of recombination give rise to vibrations of different frequency the phosphorescence spectrum will consist of three bands which decay at different rates, and which may differ widely in intensity.

The determination of the law of decay of phosphorescence upon the basis of the theory just outlined is thus seen to involve the determination of n, φ and ψ as functions of t. In the general case the solution presents difficulties that are well nigh insurmountable. The problem may be simplified, however, by an assumption, which, while doubtless not exactly true, probably gives in the majority of cases a close approximation to the actual conditions. It is assumed, namely, that $\alpha_1 = \alpha_2 = \alpha_3$, in other words the probability that a collision will result in recombination is the same for the three types of collision. In this case

$$(1) \qquad \frac{dn}{dt} = -\alpha\varphi n^2 - \alpha\psi n^2 - \alpha(1 - \varphi - \psi)n^2 = -\alpha n^2,$$

$$(2) \qquad n = \frac{1}{1/n_0 + \alpha t},$$

where n_0 is the number of positive (or negative) ions when excitation ceases.

To determine φ and ψ as functions of t it is necessary to make some assumption regarding the rate at which the free positive ions attach themselves to neutral molecules. Since the number of neutral molecules is presumably large as compared with the number of ions, it is reasonable to assume that the rate at which new groups are formed is proportional to the number of ions that are still free to enter into such combination. In other words we may assume $k_1\varphi n$ and $k_2\varphi n$ as the rates of formation of new groups of the two possible types. Since the positive ions, whether free or attached, are also recombining with the negative ions we have

$$(3) \qquad \frac{d}{dt}(\varphi n) = -\alpha\varphi n^2 - (k_1 + k_2)\varphi n.$$

While positive ions will occasionally break loose from the groups to which they have attached themselves and return to the "free" condition, this will occur only rarely on account of the sluggishness with which these ions move. I have therefore omitted as negligibly small the positive term due to this cause which should appear in the right hand member of equation (3). At high temperatures, however, and perhaps under other special conditions, the omision of this term will no longer be permissible. If the molecular movements are sufficiently violent, due to high temperature or other causes, the formation of groups may even be prevented altogether. Such cases will be considered later.

Equation (3) may be written

$$\frac{d}{dt}(\varphi n) = \varphi\frac{dn}{dt} + n\frac{d\varphi}{dt} = -\alpha\varphi n^2 - (k_1 + k_2)\varphi n.$$

Remembering that $dn/dt = -\alpha n^2$ this becomes

$$\frac{d\varphi}{dt} = -(k_1 + k_2)\varphi,$$

$$\varphi = \varphi_0 e^{-mt},$$

where $m = k_1 + k_2$ and φ_0 is the value of φ for $t = 0$.

In the case of the positive ions that are attached to neutral molecules of the active substance recombinations are occurring with negative ions at the rate $\alpha\psi n^2$, while new groups are being formed by the attachment of free positive ions at the rate $k_1\varphi n$

$$\therefore \frac{d}{dt}(\psi n) = -\alpha\psi n^2 + k_1\varphi n$$

or

$$(5) \qquad \psi\frac{dn}{dt} + n\frac{d\psi}{dt} = -\alpha\psi n^2 + k_1\varphi n.$$

Since

$$\frac{dn}{dt} = -\alpha n^2$$

we have

$$\frac{d\psi}{dt} = k_1\varphi = k_1\varphi_0 e^{-mt},$$

$$\therefore \psi = -\frac{k_1\varphi_0}{m}e^{-mt} + \text{const.}$$

Putting ψ_0 for the value of ψ when $t = 0$

$$(6) \qquad \psi = \psi_0 + \frac{k_1\varphi_0}{m}(1 - e^{-mt}).$$

For the intensities of the three constituents of the phosphorescent light we have therefore

$$I_1 = p_1\alpha\varphi n^2 = \frac{p_1\alpha\varphi_0 e^{-mt}}{(1/n_0 + \alpha t)^2},$$

$$I_2 = p_2\alpha\psi n^2 = \frac{p_2\alpha[\psi_0 + k_1\varphi_0/m(1 - e^{-mt})]}{(1/n_0 + \alpha t)^2},$$

$$I_3 = p_3\alpha(1 - \varphi - \psi)n^2 = \frac{p_3\alpha[1 - \psi_0 - k_1\varphi_0/m - k_2\varphi_0/m \cdot e^{-mt})]}{(1/n_0 + \alpha t)^2}.$$

Since we have usually plotted the reciprocal square root of the intensity of phosphorescence it will be convenient to use the same procedure here.

$$1/\sqrt{I_1} = \frac{1}{\sqrt{p_1\alpha\varphi_0}}e^{\frac{1}{2}mt}(1/n_0 + \alpha t),$$

$$1/\sqrt{I_2} = \frac{1/n_0 + \alpha t}{\sqrt{p_2\alpha[\psi_0 + k_1\varphi_0/m(1 - e^{-mt})]}},$$

$$1/\sqrt{I_3} = \frac{1/n_0 + \alpha t}{\sqrt{p_3\alpha[1 - \psi_0 - k_1\varphi_0/m - k\varphi_0/m \cdot e^{-mt}]}}.$$

Replacing certain groups of constant terms by single letters for brevity these expressions may be written

$$1/\sqrt{I_1} = A_1\varepsilon^{\frac{1}{2}mt}(1/n_0 + \alpha t),$$

$$1/\sqrt{I_2} = \frac{1/n_0 + \alpha t}{\sqrt{A_2 - B_2e^{-mt}}},$$

$$1/\sqrt{I_3} = \frac{1/n_0 + \alpha t}{\sqrt{A_3 - B_3e^{-mt}}}.$$

If a curve is plotted for $1/\sqrt{I_1}$ in accordance with the above equation it is found to be of the type shown in Fig. 72 for $\gamma = 0$. The curve for $1/\sqrt{I_2}$ and $1/\sqrt{I_2}$ is concave *upward* during the early stages of decay, becoming practically straight when t is so large as to make e^{-mt} inappreciable.

No decay curves corresponding to either of these types has been observed. It must be remembered, however, that the effects of absorption, diffusion, and irregular distribution have been neglected in the present discussion. It is probable that one or more of these sources of disturbance are present, in which case the theoretical decay curves would be modified in such a way as to make them correspond more nearly with the curves actually observed. If m is large, for example, the curve for $I_2^{-\frac{1}{2}}$ will be straight except in the immediate neighborhood of $t = 0$. Irregularities in the distribution of the active substance would then produce a deviation from linearity, as discussed on pp. 377–381. It appears to me probable that the observed facts, in the cases of phosporescence thus far studied, are best explained in this way. It is interesting to note, however, that curves may be obtained as the result of ionic grouping which agree very closely with the experimental curves, even on the assumption of a uniform distribution of the active material. If, for example, I_1 and I_2 *both* contribute to the phosphorescence, while I_3 is zero or negligible

$$I = I_1 + I_2 = \frac{p_2 a[\psi_0 + k_1\varphi_0/m\cdot(1 - e^{-mt})] + p_1 a\varphi_0 e^{-mt}}{(1/n_0 + at)^2},$$

$$1/\sqrt{I} = \frac{1/n_0 + at}{\sqrt{A + Be^{-mt}}}, \tag{7}$$

where

$$A = p_2 a\left(\psi_0 + \frac{k_1\varphi_0}{m}\right),$$

$$B = p_1 a\varphi_0 - p_2 a\frac{k_1\varphi_0}{m}.$$

In case all three modes of recombination contribute to the phosphorescence we obtain a similar expression for $I^{-\frac{1}{2}}$ except that A and B now have the values

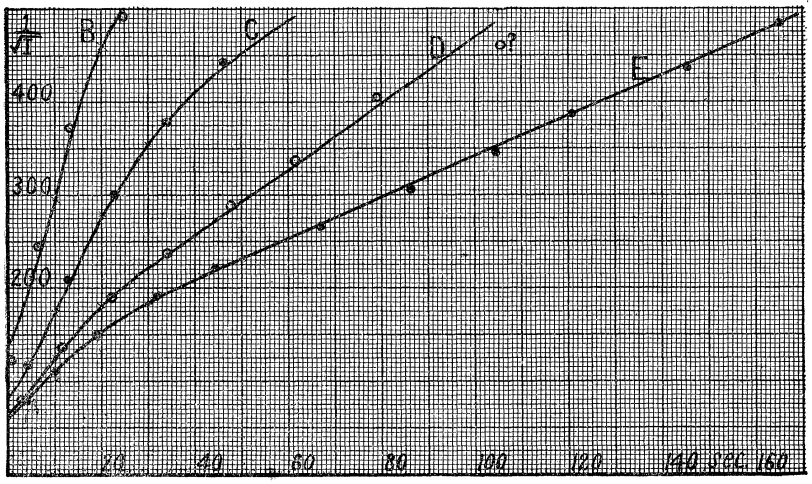

Fig. 71. Observed decay curves for different durations of excitation compared with curves computed from the equation

$$\frac{1}{\sqrt{I}} = \frac{1/n_1 + at}{\sqrt{B(\gamma + e^{-mt})}}.$$

The times of excitation and the relative numerical values of the constants used in computation are as follows:

Curve.	Excitation.	γ	$1/N_0$	$\sqrt{B}$	
E	60 sec.	0.36	72	1	
D	37 "	0.4	167	2.18	$a = 4.8$
C	11.6 "	0.1	336	4	$m = 0.16$
B	5.4 "	0.1	650	4.35	

$$A = p_2 a\left(\varphi_0 + \frac{k_1\varphi_0}{m}\right) + p_1 a\left(1 - \varphi_0 - \frac{k_1\varphi_0}{m}\right),$$

$$B = p_1 a\varphi_0 - p_2 a\frac{k_1\varphi_0}{m} - p_3 a\frac{k_2\varphi_0}{m}.$$

In Fig. 71 several curves have been plotted for $I^{-\frac{1}{2}}$ by means of this equation. Values of the constants have been determined by trial so as to make these curves correspond as nearly as possible with the series of experimental curves obtained with Sidot blende by varying the time of excitation.[1] Observational points are indicated by circles. It will be seen that, except in the case of one curve, the agreement is highly satisfactory.

To give an idea of the character of the decay curves which might result from the presence of grouped ions (disturbances due to diffusion, absorption, etc., being neglected) we may write equation (7) in the form

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{B}}\cdot\frac{1}{\sqrt{\gamma + e^{-mt}}} = \frac{(1/n_0 + at)}{\sqrt{B}}T,$$

where

$$T = \frac{1}{\sqrt{\gamma + e^{-mt}}} \quad \text{and} \quad \gamma = A/B.$$

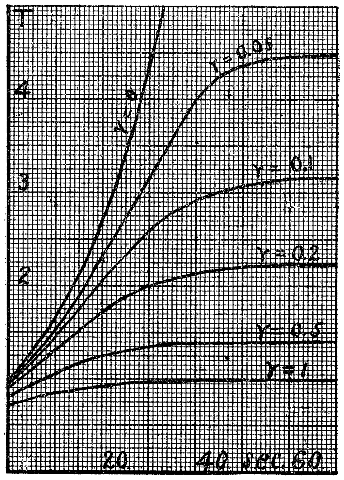

Fig. 72. Curves showing the relation between T and t for different values of γ where

$$T = \frac{1}{\sqrt{\gamma + e^{-t}}}.$$

The first factor alone plots as a straight line. The deviation from linearity in the curve for $I^{-\frac{1}{2}}$ is therefore determined by the second factor T. Putting $m = 1$ I have computed T as a function of t for several values of γ, the results being plotted in Fig. 72. For values of γ ranging from 0.1 to 5.0 the curves are of such a character as to correspond with the experimental curves for $I^{-\frac{1}{2}}$. But for smaller values of γ a double curvature is shown which is not found in any

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[1] Nichols and Merritt, PHYSICAL REVIEW, Vol. 23, p. 45, Fig. 44.

of the curves that we have determined. There is, however, an indication of such a double curvature in some of the results of Pierce. It is clear that disturbances, due, for example, to irregularities in the distribution of the active material, might so alter the early part of the curve as to eliminate any peculiarities of this nature. In fact there is at present so much uncertainty regarding the relative importance of the different factors that influence the form of the curve for small values of t that it is difficult to reach any definite conclusions concerning this part of the curve. Experiments bearing upon the distribution of the active material, the rate of diffusion of the ions, and related matters are greatly needed.

HYSTERESIS, TEMPERATURE EFFECTS, ETC., EXPLAINED BY IONIC GROUPING.

To account for the hysteresis exhibited by phosphorescent substances, in other words, the effect of a previous exposure upon the phosphorescence produced by a given excitation, it is necessary to consider the essential difference that probably exists between the groups formed by the union of positive ions with neutral molecules of the active substance and those formed by the attachment of positive ions with molecules of the solvent. For the sake of brevity, as well as for reasons that will appear shortly, we shall refer to the former as *favorable groups* and to the latter as *unfavorable groups*.

We have already introduced the assumption that light is produced by the recombination of a negative ion with a favorable group, while the recombination of the unfavorable groups, at least in some cases, gives out no light. A difference is to be expected also in the behavior of the neutral molecules that result from recombination in the two cases. A favorable group consists in a positive ion attached to at least one neutral molecule *of the same sort.* It seems natural to expect that forces similar to those that hold together the molecules of a crystal may cause this grouping to persist even after recombination has occurred. In the case of the unfavorable groups this tendency to persist can scarcely be present in the same degree if at all.

The condition of the phosphorescent substance is thus different after phosphorescence has ceased from what it was before excitation. The difference consists in the presence in the mass of a larger number of grouped molecules of the active substance, which are so intimately connected that when one member of the group is dissociated during subsequent excitation its positive ion is in a position to form immediately one of the groups favorable to phosphorescence. After the substance has been excited it is therefore in a condition which enables a subsequent excitation to produce a larger proportion of favorable groups than would be produced by a similar excitation of the fresh substance. In other words the ψ_0 of equation (7) is increased.

During excitation we have dissociation and recombination taking place at the same time; and the recombinations that occur during excitation will bring about the same change in the condition of the substance that we have assumed during decay. The value of ψ_0 will therefore increase with the duration of exposure to the exciting rays. Prolonged excitation, up to the point where saturation is reached, also increases the number of ions, *i. e.*, the value of n_0. A series of decay curves for different times of exposure should therefore resemble the curves of Fig. 71, which are computed from equation (7) by giving progressively increasing values to the constants ψ_0 and n_0.

The new condition in which a substance is left after phosphorescence can scarcely be one of complete stability. The natural and stable arrangement of the molecules is that of the substance before it has been disturbed by the action of light. It is to be expected, therefore, that there will be a more or less gradual return to the normal state after the light has ceased to act. The recombination of the ions produced by excitation, with the accompanying phosphorescence, forms only one stage in the complete return to the normal state, and is followed by a more gradual breaking down of the molecular groups resulting from recombination. We thus have an explanation of the effect of rest. The effect of exposure to infra-red rays and of elevation of temperature is to hasten the return to the normal state by increasing the rate at which these groups disintegrate.

To account for the action of the infra-red rays during excitation and decay it is only necessary to assume that these rays also have the power of breaking down the "favorable groups." In the case of Sidot blende the effect on the unfavorable groups appears to be inappreciable. Upon exposure to infra-red during decay the first result is to diminish the number of favorable groups, and to correspondingly increase the number of free positive ions. This, by itself, will not greatly alter the intensity of phosphorescence; for in the phosphorescence of Sidot blende the recombination of a free positive ion appears to be nearly or quite as effective as the recombination of a favorable group. But an increase in the number of free ions causes an increase in the rate at which unfavorable groups are formed. The positive ions that are shaken loose from the favorable groups therefore pass quickly into the inactive condition, and a rapid diminution in the intensity of phosphorescence results. The rate of decrease of course depends upon the intensity of the active rays.

If the infra-red rays are allowed to act for a short time and are then cut off, the condition of the phosphorescent substance will differ in two respects from that which it would have reached during ordinary decay: (1) the number of favorable groups is less than it would have been without the action of the longer waves; (2) the number of free ions is, at least to some extent, in excess of the normal. After the infra-red rays have ceased to act, however, the free ions will soon form groups again, either favorable or unfavorable, and the decay curve will quickly return to the standard form. But the number of favorable groups will be less than if the infra-red rays had not acted. The effect of exposure to the longer waves is simply to bring the substance quickly into the same condition that it would ordinarily acquire only after a much longer period of decay. The theory here discussed is thus seen to be incomplete agreement with the experimental results shown in Figs. 60 and 61 of the eighth article of this series.[1]

It seems probable that in some substances certain rays, presumably in the infra-red, may have the effect of breaking down the unfavorable as well as the favorable groups. In such cases exposure to these rays would probably bring about an increase in the brilliancy of phosphorescence instead of a decrease. This is said to be

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[1] PHYS. REV., Vol. 25, p. 371.

the case with certain of the phosphorescent sulphides. The same effect would be produced in substances where the recombination of a free positive ion gives out more light than that of an attached ion ; *i. e.*, where $p_1 > p_2$.

In cases like that of Sidot blende the form of the decay curve as modified by exposure to infra-red rays may be determined as follows :

We shall assume that the rate at which favorable groups are broken down is proportional to the intensity of the active rays I_r and the number of favorable groups present (ψn). We therefore have

$$\frac{d}{dt}(\psi n) = -a\psi n^2 - R\psi n + k_1\varphi n \tag{8}$$

where R is proportional to I_r.

The destructive effect of the infra-red is so great, even for rays of small intensity, while k_1 is so small, that the last term $k_1\varphi n$ may in general be neglected. It is only in the case of exposure to very weak rays, or with substances which show the infra-red effect in small intensity, that the omission of this term will lead to appreciable errors. Equation (8) therefore becomes

$$\psi\frac{dn}{dt} + n\frac{d\psi}{dt} = -a\psi n^2 + n\frac{d\psi}{dt} = -a\psi n^2 - R\psi n,$$

$$\frac{d\psi}{dn} = -R\psi,$$

$$\psi = \psi_1\epsilon^{-Rt}; \tag{9}$$

t is here reckoned from the time when exposure to the infra-red rays begins. If we take t as the time that has elapsed since the end of excitation we have

$$\psi = \psi_1 e^{-R(t-t_1)}$$

where t_1 is the time at which the longer waves begin to act and ψ_1 is the value of ψ at this time.

To determine the number of free positive ions φn after the infra-red rays begin to act we have the equation

$$\frac{d}{dt}(\varphi n) = -a\varphi n^2 + R\psi n - k_2\varphi n,$$

$$\varphi\frac{dn}{dt} + n\frac{d\varphi}{dt} = -\varphi a n^2 + n\frac{d\varphi}{dt} = -a\varphi n^2 + R\psi n - k_2\varphi n,$$

$$\frac{d\varphi}{dt} + k_2\varphi = R\psi = R\psi_1 e^{-Rt},$$

$$\varphi = \varphi_1 e^{-k_2(t-t_1)} - \frac{R\psi_1}{k_2 - R}e^{-R(t-t_1)}. \qquad (10)$$

An interesting special case, corresponding to the experimental conditions in much of our work with Sidot blende, is that in which the exposure to infra-red rays begins at once when excitation ceases, *i. e.*, $t_1 = 0$. In this case

$$\varphi_1 = \varphi_0, \quad \psi_1 = \psi_0, \quad \varphi = \varphi_0 e^{-k_2 t} + \frac{R\psi_0}{k_2 - R}(e^{-Rt} - e^{-k_2 t}), \quad \psi = \psi_0 e^{-Rt},$$

$$I = p_1 a\varphi n^2 + p_2 a_2 \psi n^2 = (A_1 e^{-Rt} + B_1 e^{-k_2 t})n^2,$$

where

$$A_1 = p_2 a_2 \psi_0 \frac{k_2}{k_2 - R}, \quad B_1 = p_1 a_1\left(\varphi_0 - \frac{R\psi_0}{k_2 - R}\right).$$

For the special case where $p_1 a_1 = p_2 a_2$,

$$\frac{1}{\sqrt{I}} = \eta = \frac{1/n_0 + at}{\sqrt{\frac{\psi_0 k_2}{k_2 - R}\varepsilon^{-Rt} + \left(\varphi_0 - \frac{R\psi_0}{k_2 - R}\right)e^{-k_2 t}}}.$$

If the infra-red rays are intense so that R/k_2 is large.

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{k_2\psi_0/R \cdot e^{-Rt} + (\psi_1 + \psi_0)e^{-k_2 t}}},$$

and in the extreme case where R may be treated as infinite

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{(\varphi_0 + \psi_0)e^{-k_2 t}}}.$$

This gives a curve having the same form as the observational curve shown in Fig. 64, which is reproduced from the preceding article of this series. The data of Figs. 65, 66 and 67[1] will be found to give curves of the same form for $1/\sqrt{I'}$, but the curve has been plotted only in the case of Fig. 64.

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[1] Phys. Rev., Vol. 25, p. 362.

At high temperatures the increased activity of the molecular movements will tend to prevent the formation of groups, or rather to destroy the groups almost as quickly as they are formed. All those phenomena that depend upon the existence of groups will therefore become less prominent as the temperature rises. Sooner or later a temperature will be reached where groups can no longer exist. At temperatures above this point we should expect no effect from exposure to the infra-red, and all hysteresis effects should disappear. The experiments of Pierce show that hysteresis still persists in Balman's paint at 133° C. No other data bearing upon this point are available.

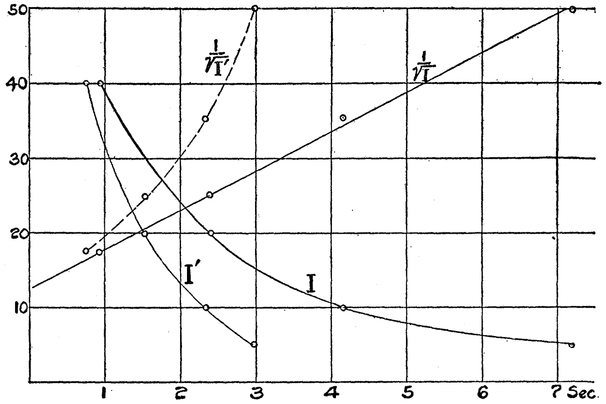

Fig. 64. Decay curves with and without infra-red. $\lambda = 0.546 \mu$.

It would be a matter of no great difficulty to develop the theory of ionic groups in much greater detail than has here been attempted, for when uncomplicated by the effects of irregular distribution and diffusion the theory lends itself readily to analytical treatment. But in view of the small amount of experimental data that are available for testing the conclusions it seems inadvisable to carry the development further at present.

SUMMARY.

In the case of a homogeneous substance having only one band in its phosphorescence spectrum and uniformly excited throughout, the dissociation theory first suggested by Wiedemann and Schmidt leads to a linear relation between t and $I^{-\frac{1}{2}}$ during the decay of phosphorescence.[1] The observed decay curve, however — *i. e.*, the curve obtained when $I^{-\frac{1}{2}}$ is plotted as a function of t — usually shows a more or less sharp curvature in the early stages of decay, and only later becomes straight. Using the dissociation theory as a basis the present paper discusses first the influence upon the decay curve of various disturbing factors, such as absorption of the exciting and emitted light, diffusion, etc. The paper then discusses the effect upon the various phenomena of phosphorescence of the formation of complex ions, which are assumed to be produced by the attachment of simple ions to neutral molecules; and after the introduction of certain hypotheses regarding the behavior of such ionic groups, an analytical theory is developed.

Briefly the results of the discussion are as follows:

1. Data thus far obtained for the decay of phosphorescence in no case definitely contradict Becquerel's explanation of the form of the decay curve, viz., that the curvature is due to the existence of two bands in the phosphorescence spectrum. Several objections to this explanation are, however, mentioned. For example, the fact that the decay curve has the usual form even when precautions are taken to study only a single band; the fact that the decay curve is of the same type for all substances thus far studied; and the fact that Becquerel's explanation takes no account of hysteresis phenomena, the effect of infra-red rays, etc.

2. It is shown that lack of transparency in the phosphorescent substance, resulting in the absorption of either the exciting light or the emitted light or both, will cause a slight curvature in the decay curve. But the effect can under no circumstances be sufficient to account for the observed deviation from linearity.

3. Lack of uniformity in the distribution of the active material throughout the mass of the phosphorescent substance will cause a deviation from linearity corresponding to that actually observed. Under certain conditions the effect is the same as though the substance possessed two or more bands, coincident as regards wave-length, but differing in rate of decay. It is pointed out that such a lack of homogeneity is to be expected from the method of preparation of phosphorescent substances, and has a great deal to do with the complexity of the phenomena.

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[1] Nichols and Merritt, PHYS. REV., Vol. 22, p. 279, 1906.

4. Diffusion of the ions will produce effects similar to those caused by irregularities in the distribution of the active material without diffusion, but the effects will be more marked. An explanation of hysteresis effects may also be based upon the presence of diffusion.

5. The assumption of complex or grouped ions is shown to lead to a law of decay which agrees closely with experiment. Ionic grouping also accounts satisfactorily for the dependence of the decay curve upon the duration of excitation and the previous history of the substance, and for the effect of exposure to the infra-red.

The preceding discussion appears to justify the conclusion that the dissociation theory proposed by Wiedemann and Schmidt is able to account satisfactorily for all the phenomena of phosphorescence thus far studied. Additional quantitative data are greatly needed, however, in order to make possible the further development of the theory. The present difficulty is not so much in accounting for the observed facts as in discriminating between different hypotheses that are at present equally plausible, and in deciding to what extent various recognized sources of disturbance are of importance. The form of the decay curve, for example, may be accounted for equally well by the assumption of two bands, by an irregular distribution of the active substance, by diffusion, or by ionic grouping, and is unquestionably modified by absorption. No quantitative test of either explanation is possible until the relative importance of the other factors is known. It may be, for instance, that diffusion does not occur at all; and it is possible, but not probable, that the disturbances due to lack of homogeneity are of no significance. Experiments that will furnish a definite answer to questions of this sort are of the greatest importance in the development of this or any other theory of phosphorescence.