STUDIES OF LUMINESCENCE.

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IV. THE INFLUENCE OF LIGHT UPON THE ABSORPTION AND ELECTRICAL CONDUCTIVITY OF FLUORESCENT SOLUTIONS.[1]

IT is a characteristic of fluorescent substances that the light emitted during fluorescence is different in color from the light that the substance absorbs and to which its fluorescence is due. This difference may be exhibited graphically by plotting the transmission and fluorescence spectra of the substance in question upon the same diagram, as in Fig. 22. It will be noticed that the brightest

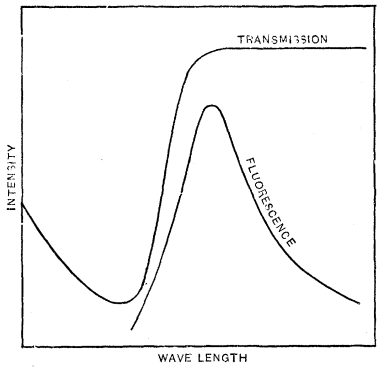

Fig. 22.

fluorescence does not correspond with the region of greatest absorption, but is displaced toward the longer wave-lengths. In all the cases thus far studied by the writers[2] the two spectra overlap, and the fluorescence spectrum extends into the region of strong absorption. But it can also be followed for a considerable distance beyond the extreme infra edge of the absorption band. A fluorescent sub-

[1] A preliminary account of the experiments described in this paper was presented to the American Physical Society at the Washington meeting, April 22, 1904. An abstract appeared in the PHYSICAL REVIEW, Vol. 18, p. 447, June, 1904.

[2] PHYSICAL REVIEW, Vol. 18, p. 403, and Vol. 19, p. 18.

stance is thus able to emit light which, under ordinary conditions, it does not absorb; and no simple relation between absorption and emission can be recognized. In consequence of this fact fluorescent substances are usually excepted from the application of Kirchoff's Law.

This seeming lack of a simple relation between absorption and emission has made it difficult to form a picture of the molecular processes that accompany fluorescence. For, whatever may be the condition of the fluorescent substance, it does not seem possible that its molecules can be in the state of vibration corresponding to the fluorescence spectrum without also possessing the power of absorbing by resonance the same rays that they emit. In seeking an explanation of this difficulty it must be remembered that absorbing power is usually determined when the substance under investigation is *not* excited to fluorescence. The absorbing power *during* fluorescence may be quite different, for it seems not improbable that the same rays that excite fluorescence also produce a temporary change in absorbing power of a fluorescent substance. If such a change really occurs the difficulty mentioned above may prove to be only an apparent one, and the absorption, as determined during fluorescence, may be found to bear to the emission spectrum a relation which is at least similar to that called for by Kirchoff's Law.

A change in absorbing power during fluorescence has been observed in the case of uranium glass by Burke,[1] who found a considerable increase in the absorption when the glass was brightly fluorescent.

The writers have recently undertaken a study of the effect of fluorescence upon absorption in the case of other fluorescent substances, and have detected a well marked increase in absorbing power during fluorescence in each of the three substances thus far tested. The methods employed and the results obtained are described in the first part of the present paper. In attempting to interpret the results of this investigation we were led to suspect that fluorescence is accompanied by a temporary dissociation of the active molecule or ion, similar perhaps to the dissociation produced in gases by the action of Röntgen rays, and that the change in absorp-

[1] John Burke, Philosophical Transactions, Vol. 191A, p. 87, 1898.

tion during fluorescence is due to the presence in the solution of the products of this dissociation.[1] Since such dissociation would in all likelihood bring about an increase in electrical conductivity, it seemed desirable to study the possible influence of light upon the conducting power of fluorescent solutions. The negative results obtained by those who had previously attempted to detect a change in conductivity in solutions due to illumination showed that such an effect, if present at all, must be quite small. We have, however, obtained conclusive evidence of an increase in electrical conductivity during fluorescence in the case of each of the five substances thus far tested. The second and third parts of the paper are devoted to a description of the experiments on this subject and a statement of the considerations which led us to undertake them.

I. THE INFLUENCE OF FLUORESCENCE UPON ABSORBING POWER.

In the experiments of Burke, to which reference has already been made, the light used was that due to the fluorescence of a piece of uranium glass, and the absorption of the rays from this source by a second piece of uranium glass was determined photometrically. The absorption was found to be increased nearly 50 per cent. when the second piece of uranium glass was excited to bright fluorescence. While the method employed by Burke is a sensitive one, and well adapted to demonstrating the existence of the effect sought, it does not lend itself readily to a detailed study of the subject. It appeared to us desirable to determine not only the increase in total absorption, but also the influence of fluorescence on the form of the absorption spectrum. With this object in view we have determined the change in absorbing power for a number of different wave-lengths throughout the region in which the effect was observable, using for this purpose a Lummer-Brodhun spectrophotometer. Three fluorescent solutions have thus far been tested, namely, fluorescein in water, eosin in alcohol, and rezazurin in alcohol. Each of these solutions showed an increase in absorbing power during fluorescence, the effect being most marked in the case of fluorescein. For this reason the study of the subject has

[1] The dissociation here considered can hardly be of the usual electrolytic type, for it seems to be well established that with many substances fluorescence is an ionic property, and can be excited only after electrolytic dissociation has already occurred.

been carried further in the case of the latter substance than with either of the other two.

The arrangement of apparatus is shown in Fig. 23. The fluorescent solution, contained in a rectangular glass cell, *C*, was placed in front of the slit of the collimator. The solution was excited to fluorescence by rays from the source *E*, which usually consisted of a bank of four acetylene flames. When it was desired to measure the absorption of the solution without fluorescence a screen was interposed between *E* and *C*. A block of magnesium carbonate, *M*, reflected a portion of the light from *E* through the cell containing the fluorescent solution into the collimator slit, *S*. By altering the distance of *M* from *S* the transmitted light could be adjusted to any desired intensity. In some of our earlier experiments the block of magnesium carbonate was removed and direct sunlight was used. The comparison source was an acetylene flame, *A*, whose rays were reflected from a second block of magnesium carbonate, *M'*. The spectrophotometer was used in the ordinary way, *i. e.*, without a lens in the eye piece.

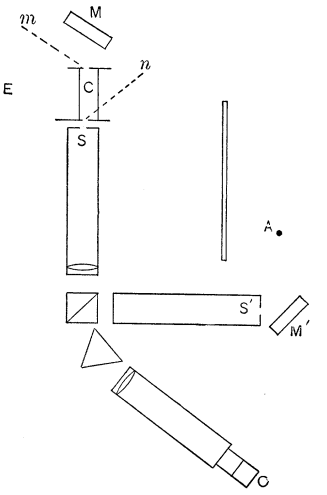

Fig. 23.

To determine the increase in absorption due to fluorescence the following three readings were required for each wave-length studied :

1. *Transmission* (*T*).—An opaque screen was placed between *E* and *C* to prevent fluorescence. The slit *S'* was then opened or closed until the two parts of the field, as seen from *O*, appeared equally illuminated. The width of the slit, as read from the drum of its micrometer screw, was then proportional to the intensity of the transmitted light. We shall designate this reading by *T*.

2. *Fluorescence* (*F*).—The screen was removed from between *E* and *C* and placed between *C* and *M*, so that the only light reaching the slit was that due to the fluorescence excited by the rays from *E*. The setting of *S'* for equal illumination was then a measure of

the intensity of fluorescence for the particular spectral region studied.

3. *Transmission and Fluorescence Combined* (C).—Both screens were removed. In this case the light entering the slit consisted partly of rays from M which had been transmitted by the solution and partly of rays originating in the solution itself by fluorescence.

The width of the slit S remained the same during all of the above readings.

If the absorbing power of the solution is not altered by fluorescence it is clear that the sum of the first two readings should be equal to the third except for accidental errors of observaton. But if fluorescence brings about an increase in absorbing power this equality can no longer hold; for, while the amount of light reaching the slit due to fluorescence will be the same in the third measurement as in the first, the light from M, which must pass through the cell, will be less intense than that observed without fluorescence. In this case therefore $F + T$ is less than C. In fact C may be looked upon as the sum of two parts F and T', where T' is the amount of light from M that is transmitted by the solution when the latter is excited to fluorescence. Since $F + T' = C$ we have

$$F + T - C = T - T'.$$

The quantity $F + T - C$ is therefore a measure of the increase in absorption due to fluorescence.

A single determination of the increase in absorption thus requires three photometric settings, each of which is subject to the usual accidental errors of observation; and the quantity sought, which is in all cases small, is obtained as the difference of two quantities that are relatively large. The results will therefore be largely affected by errors, whether accidental or systematic, in the individual readings. For this reason it was necessary to consider the possible sources of error with especial care. The recognized sources of error and the means taken to avoid them are discussed below.

Errors of Observation.—In order to reduce the effect of accidental errors each set of readings was repeated several times. In some cases as many as ten settings were made for each of the three quantities T, F, and C. The advantage to be gained by repetition was limited, however, by eye fatigue and the resulting loss of sensi-

tiveness. In making a series of determinations extending throughout the spectrum we found it inadvisable to repeat the settings more than four times. The settings were usually made by one observer, while the indications of the micrometer screw were read and recorded by the other.

Fluctuations in the Source of Light.—In our early experiments intense fluorescence was obtained by the use of the arc as an exciting source. Unfortunately the irregular fluctuations were found to neutralize entirely the advantage of great intensity. Sunlight was equally unsatisfactory. In most of our work a bank of acetylene burners was used to excite fluorescence, and with this source no further trouble due to variations in intensity was noticed.

Stray Light. — The effect of this source of error will depend upon the origin of the stray light and the manner in which it enters the instrument. Light reflected into the slit S by dust particles in the cell will cause no error in the final result; for the effect of light due to this cause will be to increase C and $T + F$ by equal amounts. Stray light from E which reaches the slit by any other route will be equally harmless, provided it is suppressed by the screen between E and C (Fig. 23) during the measurement of transmission. But light reaching the interior of the instrument in such a way as to remain nearly constant during the measurement of T, F, and C may lead to serious error. In this case each of these three readings will be too large, and the quantity $T + F - C$ will be in error by the amount of the stray light. To prevent any stray light from entering the instrument through the slit S opaque screens were arranged as shown, in part, in Fig. 23. The purpose of the large screen was to cut off all light from the comparison source. The cell C was completely covered with black paper with the exception of the face toward E and the two narrow openings, m and n, for the transmitted light. To prevent light entering the telescope after diffuse reflection from the prisms the whole instrument was covered with several layers of dark cloth, while screens were so placed as to prevent the direct rays from E or A (Fig. 23) from reaching any part of the spectrophotometer. The experiments were performed in a room with black walls, the only light in the room being that from the flames used in the measurements. After these precautions

were taken it was found that when screens were placed between E and C and between M and C no trace of light could be detected in the spectrophotometer field. We feel confident therefore that the errors due to stray light are very small.

Zero Point. — The zero point of the micrometer screw used in measuring the width of the slit S' was determined by placing an acetylene flame immediately in front of the slit, so as to illuminate it brightly, and then closing the slit until no light could be detected. It is clear that an error in this zero point would make each of the readings T, F, and C incorrect by the same amount, so that the result $T + F - C$ would be subject to the same error as that made in determining the zero point. The setting for zero point was repeated many times, and the agreement of the different readings was such as to convince us that the error could not exceed half a division.

Other less important sources of error, such as irregularities in the screw, "lost motion," etc., require no special discussion.

Dependence of Fluorescence Absorption upon the Intensity of the Incident Light.

In attempting to obtain the most favorable experimental conditions for studying fluorescence absorption (*i. e.*, the increased absorption due to fluorescence), we were at first led astray by assuming that absorption in a fluorescent solution takes place in accordance with the same laws that hold in ordinary optically perfect media. We expected that the effect of fluorescence would be to increase the *coefficient of absorption* without altering the usual exponential law. If this were true the percentage absorption would be constant for a given solution and a fixed intensity of fluorescence, while the actual amount of light absorbed would increase with the intensity of the incident light. If aI is the absorption under ordinary conditions, $a'I$ the absorption during fluorescence, and I the intensity of the incident light we have

$$T = I(1 - a) \qquad T' = I(1 - a')$$
$$T + F - C = T - T' = I(a' - a).$$

The quantity determined by our measurements is therefore

$I(a' - a)$, and, *if* a' *is independent of* I, it is clear that the best experimental conditions are attained when both the fluorescence and the incidence light, I, are made as great as possible.

Our early experiments, in which the conditions were chosen in accordance with the considerations just stated, gave results that were often discordant. For example, a preliminary set of readings, which happened to be made with I rather small, had indicated a well-marked increase in absorption; *i. e.*, the difference between C and $T + F$ was a large fraction of T. With the expectation of making the difference greater, and so increasing the accuracy of the determinations, the measurements were repeated with the intensity of the incident light largely increased. To our surprise the difference between $T + F$ and C was no larger than before. In fact, the errors of observation sometimes made it appear questionable whether there was any change at all due to fluorescence. We were at first inclined to ascribe the unsatisfactory results to irregular fluctuations in the intense sources of light that were used in our early experiments. But even after we had been forced to abandon the sun and the electric arc as sources, and had adopted acetylene flames throughout, no gain resulted from increasing the intensity of the incident light.

A series of measurements undertaken to determine the dependence of the effect studied upon the intensity of the incident light has since convinced us that the absorption of light in a fluorescent solution does not occur in accordance with the usual laws of absorption. The results of this series of measurements are contained in Table I. It will be observed that the quantity $T + F - C$ is nearly constant for all values of T; the variations are no greater than the possible errors of observation. Since T is proportional to I, we must conclude that the percentage absorption is not independent of I, but increases as I is made smaller. The total amount of energy absorbed, however, is constant throughout the range studied. It appears that when the solution is excited to fluorescence it acquires the power of absorbing a certain definite amount of energy, in addition to that absorbed under ordinary conditions, from a beam of light passing through it. The amount absorbed doubtless depends upon the intensity of fluorescence, the wave-

length of the light, and other factors; but our observations all point to the conclusion that it does *not* depend upon the intensity of the transmitted beam.

TABLE I.

Dependence of Fluorescence Absorption Upon the Intensity of the Incident Light. The measurements were made at wave-length 0.535 μ.

Transmission. T	Fluorescence. F	Transmission and Fluorescence Combined. C	Fluorescence Absorption. $T+F-C$	Percentage Fluorescence Absorption. $\frac{T+F-C}{T}$
18.4	34.6	46.3	6.7	36.4
34.9	34.6	64.2	5.3	15.2
61.0	34.9	91.2	4.7	7.7
12.9	34.5	42.0	5.4	42.0
24.7	34.6	52.8	6.5	26.3
12.7	33.8	41.5	5.0	39.4

It was unfortunately not practicable to investigate the effect for values of T still smaller than the smallest in Table I., for with such feeble illumination of the spectrophotometer field accurate settings became impossible. It is clear, however, that the quantity $T+F-C$ cannot remain constant for very small values of T; for this would mean that the energy absorbed on account of fluorescence is greater than the total energy of the incident light. It appears to us probable that something analogous to saturation occurs in the case of fluorescence absorption. As the intensity of the incident light is gradually increased from zero, the absorption due to fluorescence probably increases also until a certain maximum is reached, after which a further increase in the intensity of the incident light produces no change in the fluorescence absorption.

Relation between Fluorescence Absorption and Intensity of Fluorescence.

Although there is every reason to expect that the absorption due to fluorescence will be greater when the fluorescence is more intense, the lack of a theory of fluorescence makes it impossible to predict the quantitative relation between the two phenomena. With the object of determining this relation experimentally we have measured the fluorescence absorption of a solution of fluorescein at 0.535 μ for several different intensities of fluorescence. The fluorescence was varied by

altering the distance between the cell C (Fig. 23) and the exciting source E. By altering the position of the block of magnesium M (Fig. 23) the intensity of the transmitted light was adjusted in each case to approximately the same value.

The results are shown graphically in Fig. 24. In spite of the fact that each point plotted represents the average of several determinations, the curve obtained is far from being a smooth one. The results are nevertheless sufficient to show that fluorescence absorption is not directly proportional to the intensity of fluorescence. Here too we have to deal with something analogous to saturation. Although further experiments will be necessary to establish the

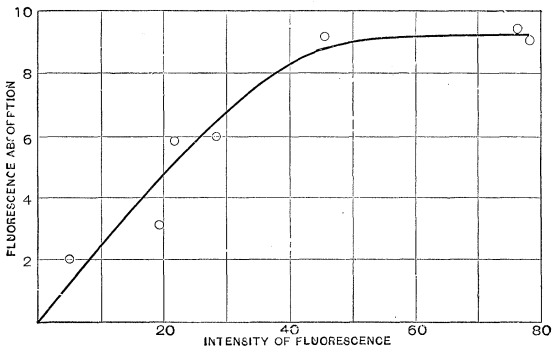

Fig. 24.

exact relation between fluorescence and fluorescence absorption, numerous observations incidental to other phases of the present investigation serve as confirmation of the general form of the curve shown in Fig. 24.

Fluorescence Absorption as a Function of Wave-Length.

In the experiments thus far described the measurements were always made in some one region of the spectrum. The wave-length of the light used, having been chosen by trial so that the fluorescence absorption was well marked, was kept constant during the whole series of determinations. To determine the florescence absorption for different wave-lengths the telescope of the spectrophotometer was shifted so as to bring different regions of the spectrum into the field, and several observations of T, F, and C were made

for each position. During these determinations the intensity of the light exciting fluorescence and the intensity of the light used for the measurement of transmission were kept as nearly as possible constant.

TABLE II.

Dilute Solution of Fluorescein. Observations to Determine Typical Fluorescence, f, and Fluorescence Absorption, A_F. Thickness of Absorbing Layer 4.9 *cm.*

Wave-Length.	T	F	C	A_F	A_F Corrected.	f Computed.
.512μ	18.1	25.9	34.3	9.7	9.5	31.6
.518	19.8	27.4	40.9	6.3	8.5	32.0
.525	22.3	26.2	41.0	7.5	6.7	29
.539	27.2	20.7	43.3	4.6	4.7	20.7
.555	27.2	15.0	39.0	3.2	3.2	15
.506	12.9	20.2	24.4	8.7	7.7	28.6
.500	8.6	12.2	17.3	3.5	3.5	20.5
.494	6.5	7.4	13.4	0.5	0.5	13.8

The results of a series of observations of this kind in the case of fluorescein are given in Table II. The solution chosen for these experiments was quite dilute, preliminary experiments having shown

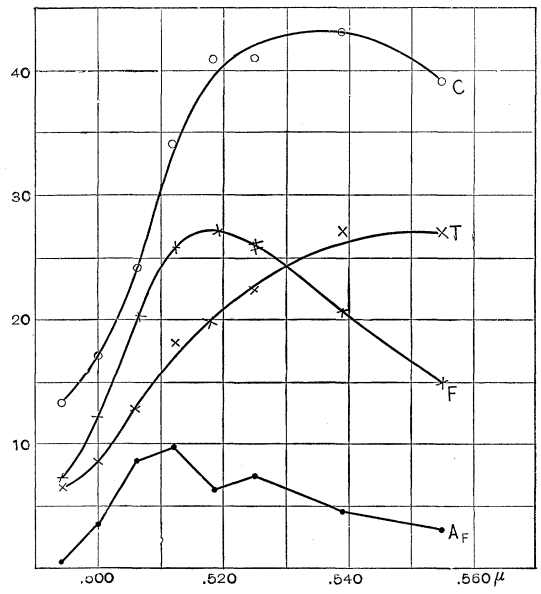

Fig. 25.

that it was difficult to obtain reliable results with more concentrated solutions, especially in the neighborhood of the normal absorption band. The data given in Table III. for T, F, C, and A_F are shown graphically in Fig. 25, the vertical scale being the same for all four curves.

In the case of observations made under constant conditions we should expect the successive readings for F, T, and C to lie upon smooth curves; and it is natural to ascribe any irregularities that appear to accidental errors. Acting upon the assumption that the conditions were constant during the observations plotted in Fig. 25,

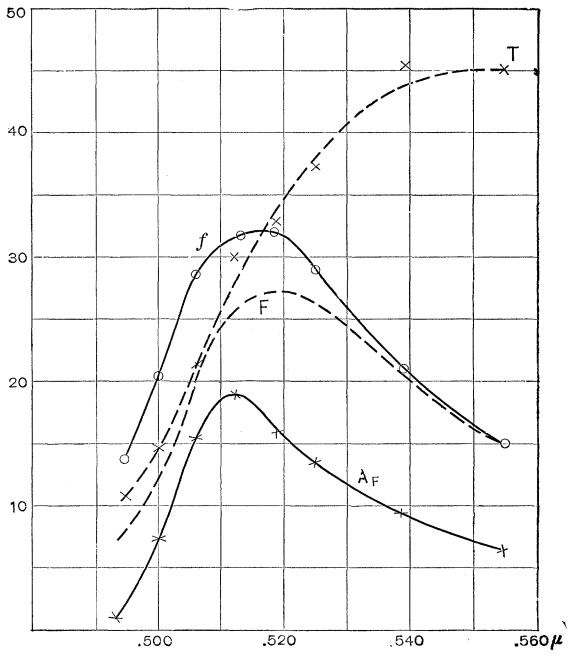

Fig. 26.

we have drawn smooth curves for T and C, as shown in the figure. By using in the computation of A_F the values of T and C that are given by these curves we obtain a curve for fluorescence absorption which is largely free from the irregularities due to accidental errors. The curve obtained in this way is plotted (to a different scale) in Fig. 26. Such a procedure would not be justified

if the irregularities in the curves were due to fluctuations in the source of light or to any similar cause. But the smooth curve obtained for F, without adjustment, affords strong evidence that the experimental conditions were really steady, and that the irregularities in the other two curves are due to errors of observation. It has been our uniform experience that accidental errors are more common in the settings for T and C than in those for fluorescence.

In spite of the irregularities in the curve for fluorescence absorption in Fig. 25 a general resemblance will be noticed between this curve and that for fluorescence (F). In the case of the smooth curve for A_F the resemblance is still more marked. This similarity in form has also been noticed in the curves plotted from numerous other sets of observations, both with fluorescein and with eosin, although it was often made less striking by our inability to keep all the conditions constant during the determination of a complete curve.

It seems probable that this resemblance between the curves for F and A_F corresponds to some real and intimate connection between fluorescence and fluorescence absorption; apparently we have to deal not with two separate effects produced in the solution by the action of the exciting light, but rather with two different manifestations of the same molecular process. If this is true we should expect the relation between the two phenomena to be more clearly brought out by a comparison between the curve for fluorescence absorption and the typical fluorescence spectrum for the solution. The latter curve depends only upon the nature of the solution and the intensity of the exciting light, while the form of the fluorescence spectrum directly observed is modified by absorption and therefore depends upon the thickness of the solution and the method of observation.[2] The relation between the typical fluorescence, f, and the observed fluorescence, F, may be derived as follows:

Let the face of the cell containing the fluorescent solution be uniformly illuminated by the exciting light, so that all portions of the solution lying between m and n (Fig. 23) are equally fluorescent. In this case light is emitted in the direction of the slit S by all portions of the solution lying between m and n. Let f be the

[1] See Figs. 4, 5 and 6 in our second paper, PHYSICAL REVIEW, XVIII., p. 403.

amount of light of a given wave-length that is emitted in this direction per centimeter. The curve that shows f as a function of the wave-length is what has been called the typical fluorescence spectrum.

The light proceeding in the direction toward S will be of increasing intensity as we pass from m to n. If its intensity at a distance x from m is I, we have

$$dI = fdx - \alpha I dx$$

where α is the coefficient of absorption. Upon integrating this equation we have

$$I = \frac{f}{\alpha} + K\varepsilon^{-\alpha x}.$$

The constant of integration K is determined by the fact that when $x = 0$, $I = 0$, so that

$$K = -\frac{f}{\alpha}.$$

Therefore

$$I = \frac{f}{\alpha}(1 - \varepsilon^{-\alpha x}).$$

The light entering the slit, which determines the measured fluorescence F, is the value of I for $x = l$, where l is the thickness of the solution.

$$F = \frac{f}{\alpha}(1 - \varepsilon^{-\alpha l}).$$

$$f = \frac{\alpha F}{1 - \varepsilon^{-\alpha l}}.$$

Since α is readily computed from the measurements of transmission we are thus able to compute the typical fluorescence from the observed fluorescence F. In the case of the experiments corresponding to Fig. 25 the percentage transmission is most conveniently computed by dividing the value of T for the wave-length in question by the value of T for $\lambda = 0.555\ \mu$. The latter point on the curve for T lies outside the absorption band, so that the transmission of the solution is complete. If the percentage transmission be denoted by θ

$$\theta = \varepsilon^{-\alpha l},$$

$$\log \theta = -\alpha l,$$

$$f = -\frac{F \log \theta}{l(1-\theta)}.$$

The typical fluorescence spectrum computed in this way is shown in Fig. 26. A comparison of this curve (f) with the smoothed curve for A_F adds support to the view that the phenomena of fluorescence and fluorescence absorption are intimately connected. But the relation between the two does not appear to be a simple one. Unless the observations are effected by more serious errors than we have any reason to suspect, the results show that fluorescence absorption does not bear a constant ratio to the intensity of the fluorescence with which it is associated. And yet this simplest possible relation between the two phenomena is the one which it seems most natural to expect. We are of the opinion that the question of the exact relation between the two curves is one which requires further experimental investigation before it can be looked upon as definitely settled.

A series of observations like those just described was made with a still more dilute solution of fluorescein with results that agree, in the main, with those stated above. In these experiments sunlight was used to excite fluorescence. The variations in the intensity of this source made it impossible to apply the method of smoothing described above; and without some means of reducing the effect of accidental errors the results were too irregular to lead to any reliable conclusions. These observations, therefore, serve merely as a check upon the general form of the curves shown in Fig. 25. The same statement may be made with reference to numerous other observations in which we were unable to maintain constant conditions throughout the complete series of readings.

In Fig. 27 we have plotted the results of a series of measurements made with a more concentrated solution of fluorescein. It will be noticed that the edge of the absorption band is much steeper than in Fig. 25, and the band extends further toward the red. Although the curve for fluorescence absorption (A_F) is similar in form to that shown in Fig. 25 its maximum is displaced toward the

longer wave-lengths. It is clear that the normal absorption of the solution exerts a modifying influence upon the increase in absorption which accompanies fluorescence.

In addition to the experiments with fluorescein a few measurements were made also with alcoholic solutions of eosin and resazurin. In the case of the latter substance the measurements were

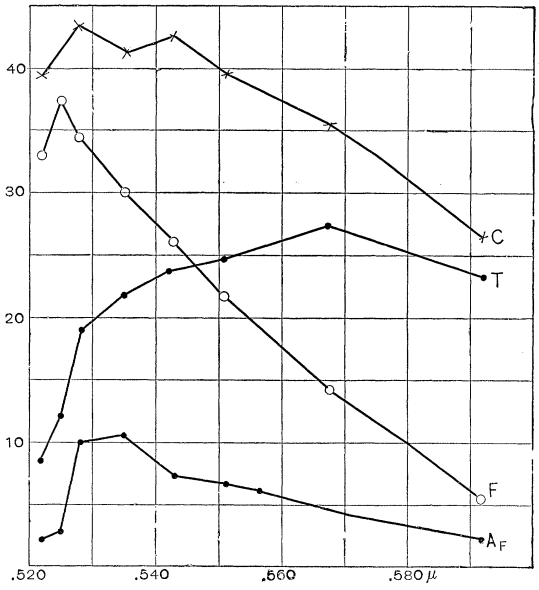

Fig. 27.

made for only a few wave-lengths, and served merely to show that the effect was present. With eosin a nearly complete curve was obtained, although not under entirely satisfactory conditions. The curve was the same general character as those obtained with fluorescein, and occupied the same position with relation to the absorption band.

II. Theoretical.

Throughout the progress of the experiments that have been described in the present paper and in those which precede it we have naturally tried to form some picture of the underlying mechanism of the phenomena studied. It is perhaps needless to say that serious difficulties have been encountered; but although we have

not succeeded in forming a wholly satisfactory picture of the molecular processes involved in fluorescence, the considerations stated below have nevertheless led us to the adoption of a working hypothesis regarding the general character of these processes which has been of considerable assistance.

In attempting to form a theory of fluorescence it is natural to turn to the other, and in some respects simpler cases of luminescence for assistance; for it is difficult to believe that the many resemblances noticeable between luminescence phenomena of different types are merely superficial. In the case of several classes of luminescence phenomena the first steps in the development of a theory have fortunately already been taken. Thermo-luminescence, for example, has been explained as the result of some chemical change in the luminescent substance, during the progress of which the molecules are thrown into such violent vibrations as to bring about the emission of light. Luminescence ceases in such cases when the change has been completed; and some outside stimulus is required, such as that furnished by cathode rays, to restore the substance to the sensitive state. Not only in this explanation of thermo-luminescence a plausible one but in several instances conclusive evidence has been found that the assumed change really occurs.

A somewhat similar suggestion has been made by E. Wiedemann in the case of phosphorescence. According to this view some change is produced in the phosphorescent substance by the action of the exciting light, and the gradual restoration of the original condition after the excitation has ceased is accompanied by luminescence. Although it has not yet been possible to determine the exact character of the assumed change, or even to demonstrate by direct tests that such a change occurs, the view suggested by Wiedemann has undoubtedly been an important aid in the more recent study of phosphorescence.

If, as seems not unlikely, the difference between phosphorescence and fluorescence is chiefly one of the duration of luminescence, the hypothesis just stated may be applied to the latter class of phenomena without essential modification, and we may assume that fluorescence is also due to some temporary change in the fluores-

cent substance. We must assume further that the return to the original condition is almost instantaneous; so that luminescence persists for only an inappreciable time after the removal of the exciting cause. According to this view fluorescence involves two processes (1) the alteration in the fluorescent substance brought about by the exciting light; (2) the spontaneous return of the modified substance to its original state. These two processes occur simultaneously; and one or both must be accompanied by the emission of light.

This view lends itself readily to an explanation of the increase in absorption that accompanies fluorescence, for it is clear that during the progress of such a change as is here assumed the substance may possess properties that are entirely different from those of the original substance. It is natural also to expect some intimate connection between fluorescence and fluorescence absorption, for the increased absorption during fluorescence is doubtless due, at least in part, to the same molecules or atoms whose vibrations bring about the emission of light. Without more detailed assumptions regarding the nature of the change produced by the exciting light it is not possible to predict the laws of fluorescence absorption, *e. g.*, the dependence of the effect upon wave-length, intensity of fluorescence, etc. But, on the other hand, the experimental study of these laws will afford a firm foundation for the further development of the working hypothesis.

The considerations which make it natural to expect a change in absorption during fluorescence apply equally well to all cases of luminescence in which there is a change in the active substance during excitation and a return to the original state during luminescence. We should therefore expect a change in absorbing power in the case of thermo-luminescence, chemi-luminescence, and phosphorescence. In fact, it seems not improbable that some modification of Wiedemann's original hypothesis may be found to be applicable to *all* classes of luminescence, and in this case we should expect every type of luminescence to be accompanied by a change in absorption. So far as we are aware, no experimental study of absorption during luminescence has been undertaken except in the case of fluorescence.

A hypothesis which assumes that luminescence results from some chemical or physical change in the luminescent substance evidently implies not only a change in absorbing power during luminescence, but also temporary alteration in the other properties of the substance. The study of these changes, if such are found to occur, offers a promising means of attacking the general problem. This field of investigation also appears to be practically untouched.

It has generally been assumed, by those who regard Wiedemann's suggested explanation of phosphorescence and thermoluminescence with favor, that the change accompanying luminescence is of a chemical nature. Various suggestions have been made regarding the character of the reactions produced by the exciting light (or other cause), and attempts are not lacking to trace a connection between luminescence and chemical constitution. It appears to us that it is desirable to take into consideration changes of a different kind, which do not involve, necessarily, any chemical action. The simplest change of this kind is dissociation. In cases of photoluminescence this is just the effect that we should expect the exciting rays to produce. We can scarcely doubt that the absorption of the exciting light is the result of resonance on the part of the molecules or atoms of the active substance; and although the vibrational energy thus imparted to the molecules is rapidly transformed by collisions into translational energy (heat) yet under favorable conditions the molecules might be thrown into such violent oscillation as to be torn apart. Since chemical activity is usually increased by dissociation, chemical changes of the usual kind might occur as a secondary effect. Many instances of increased chemical activity due by the action of light on fluorescent substances might be cited.

If we look upon light as an electromagnetic phenomenon we should expect the vibrations produced by the exciting rays to be such as tend to separate the positive and negative parts of the molecule, and the resulting dissociation would either be of the usual electrolytic type or similar to that produced in a gas by the action of Röntgen rays. In the case of fluorescence the latter type of dissociation seems most probable; but in either case, if the view outlined above is correct, fluorescence should be accompanied by an

increase in the electrical conductivity of the fluorescent substance. It was in order to test this conclusion that the experiments described in the third section of this article were begun. A more detailed discussion of the hypothesis outlined above, and of the experimental facts which tend to confirm it, is reserved for a later communication.

III. The Influence of Fluorescence upon Electrical Conductivity.

The effect of light and Röntgen rays upon the conductivity of solutions has been tested by Cunningham,[1] in the case of five solutions, one of which, namely, uranyl nitrate, was fluorescent. In the experiments with light an arc containing iron was used as a source, and the solutions were contained in a cell having a quartz window, the object being to obtain intense ultra-violet rays. Although some indication of increased conductivity was observed, the observations were rendered so uncertain by the heating effect of the rays from the arc that the author did not regard the results as reliable.

Experiments of a similar character were undertaken by Regner[2] with especial precautions against the disturbances due to the heating effect of the source. No change in conductivity as great as 0.1 per cent. could be detected, although the substances tested included those for which Cunningham had found indications of a positive result. Several fluorescent substances were tested by Regner, also with negative results.

In the paper by Burke[3] on the change in absorption due to fluorescence, mention is made of preliminary experiments upon the conductivity of fluorescent substances; but the author states that difficulties were met with which led him to abandon these experiments and to take up the study of absorbing power instead.

Our own experiments upon this subject were undertaken with the feeling that the increase in conductivity due to fluorescence was probably very small, comparable rather with the conducting power

[1] J. A. Cunningham, "An Attempt to detect the Ionization of Solutions by the Action of Light and Röntgen Rays," Proc. of the Cambridge Philosophical Society, Vol. 11, p. 431–3 (1902).

[2] Physikalische Zeitschrift, 4, 862, 1903.

[3] Burke, l. c.

produced in gases by the action of Röntgen rays than with ordinary electrolytic conductivity in solutions. In attempting to detect so small an effect it seemed advisable to work with solutions in which the normal conducting power was as small as possible. In the case of all the substances thus far tested we have therefore used absolute alcohol as a solvent.[1]

The accurate measurement of the resistance of alcoholic solutions offers considerable difficulty; for while the conducting power is too great to permit the employment of an electrometer method, such as would be used with gases, it is too small to be determined with accuracy by the methods that are generally used with aqueous solutions. No benefit was to be gained in the present experiments by increasing the cross section of the liquid tested, and so reducing its resistance; for if the thickness exceeded a rather small value the absorption of the liquid made it impossible to excite the whole mass to fluorescence. After trying a number of different methods without satisfactory results we abandoned the attempt to accurately measure the total resistance, and directed our attention to the measurement of the *change* in resistance due to illumination. The most satisfactory method that we have found for this purpose is that of the ordinary Wheatstone bridge, using a direct current and a galvanometer of high resistance.

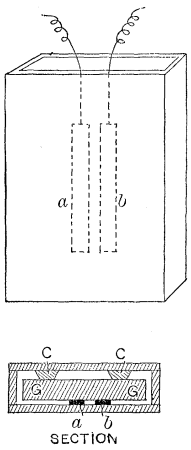

Fig. 28.

The form of the cell used to contain the fluorescent solutions is of considerable importance in its bearing upon the sensitiveness of the method. Among the galvanometers available for use with the bridge, that which seemed best suited for the work, was one having a resistance of about 10,000 ohms. It was therefore desirable to have the resistance to be tested as near to this value as other conditions would permit. On the other hand, the layer of liquid tested should be so thin that it can be excited to strong fluorescence throughout its thickness. Although we did not find it possible to satisfy both of these conditions, they were approximately met by the form of cell shown in diagram in Fig. 28.

[1] In the experiments of Cunningham and Regner the solvent was water.

The figure shows both a perspective view and a horizontal section of the cell. A thick piece of plate-glass, G, was cut of such a size as nearly to fill the cell and was held in position, tightly pressed against the two electrodes a, b (of platinum foil), by the corks C, C. Although the drawing is in other respects approximately to scale and nearly actual size, the thickness of the electrodes a, b is greatly exaggerated. The thickness of the layer of liquid between G and the walls of the tube was determined by the thickness of the electrodes and was about 0.1 mm. In the section shown in Fig. 28 the portions occupied by the solution are left unshaded. The length of the electrodes was about 20 mm. and their distance apart 2 mm.

The fluorescent substances tested were eosin, fluorescein, rhodamin, napthalin roth, and cyanin. As already stated, the solvent was in all cases absolute alcohol. The solutions were made quite concentrated, so that fluorescence was confined to a thin layer at the surface. The concentration was so adjusted as to make this fluorescent layer approximateiy 0.1 mm. thick.

The cell containing the solution to be tested was made one arm (C) of a bridge. The resistance of the arm M in series with C was in all cases 9,000 ohms, while the resistance of the third arm, R, was 5,000 ohms. The fourth arm, N, was varied until an approximate balance was obtained[1] and the apparent resistance was computed by the formula $C = MR/N$. Current was furnished by two gravity cells in series.

Polarization in the fluorescent solution made it impossible to obtain the true resistance by this method, and the apparent resistance of the cell (computed as if polarization were absent), is doubtless in error by 50 per cent. or more. But the sensitiveness of the arrangement to changes in the resistance of the test cell was high. In order to avoid disturbances due to variations in the polarization E.M.F. it was found necessary to keep both the battery circuit and the galvanometer circuit closed. Even the small change made in N during the adjustment of the balance produced a considerable alteration in the polarization, so that the adjustment often had to be continued for an hour or more before the needle of the galvanom-

[1] These resistances were chosen not because they gave the highest attainable sensitiveness, but because they were the most suitable ones that were available at the time.

eter was sufficiently steady for observations to be begun. During this time the cell was protected from the action of light by an opaque screen. When the conditions had become steady, or more frequently when the motion of the galvanometer needle was reduced to a slow uniform drift, the screen was removed and light from an arc was allowed to fall on the cell. After the effect of illumination had been noted, and when the needle had again settled down to a steady drift, the screen was replaced, and the throw of the needle in the opposite direction was observed.

In the measurement of so small an effect as that here considered it is clear that the heating effect of the rays from an arc is likely to produce serious errors, for the change in conductivity due to rise in temperature is unfortunately in the same direction as the change that we are attempting to detect. For this reason the use of the direct rays of the arc, even at the distance of a meter, was entirely out of the question. Even when a water cell was interposed in the path of the rays the needle was displaced through several hundred divisions. That this movement of the needle was due to rise in temperature, and not to the effect sought, was indicated by the fact that the change persisted after the rays were cut off; it was necessary to wait at least fifteen minutes before the original balance was approximately restored.

In order to avoid the disturbances due to rise in temperature we adopted the plan of dispersing the rays from the arc by a prism and using only those portions of the spectrum that were most effective in producing fluorescence. With this arrangement the effects observed were much smaller than before, but they were entirely free from any indication of temperature changes. Upon removing the screen, so as to illuminate that part of the fluorescent solution lying between the electrodes, a throw of the galvanometer needle was observed, and if originally free from drift the needle vibrated about a new position and finally came to rest. Continued illumination of the solution produced no increase in the deflection. Upon replacing the screen a throw in the opposite direction occurred, and the needle finally returned to its original reading. If observations were made while the needle was in motion, these throws were simply superposed upon the steady drift. In this case the effect of illumination was measured by the average of the two throws.

So far as we were able to judge, the effect produced by light reached its full value at once and ceased as soon as the light was cut off. The disturbance of the balance of the bridge was always such as to indicate an increase in the conductivity of the fluorescent solution. Upon repeating the experiments with rays from different portions of the spectrum it was found that a change in conductivity was produced only by those rays which were able to excite fluorescence in the solution tested. And so far as we could estimate the intensity of fluorescence by the eye, the rays which gave the most intense fluorescence also produced the greatest change in conductivity. In the case of eosin we were able to follow both effects to the extreme edge of the violet, while illumination by the red of the spectrum produced no effect.

In order to form an estimate of the magnitude of the change produced we observed in each case the throw caused by increasing or decreasing the resistance N by one ohm. By comparing this with the throw due to illumination, it was possible to express the observed change as a fraction of the normal (apparent) resistance. The results are given in Table III. The light used to illuminate the solution, in the case of the measurements included in the table, was that which produced the brightest fluorescence.

We have also tested in the same way one solution that was not fluorescent, namely, an alcoholic solution of fuchsin. The result was entirely negative. No change in resistance due to illumination

TABLE III.

Increase in Electrical Conductivity due to Fluorescence.

Substance.	N	Apparent Resistance of Solution.	Throw Produced by Illumination.	Throw Produced by Increasing N by 1 Ohm.	Increase in Conductivity Due to Illumination.
Eosin.	155	300,000	57 mm.	33 mm.	1.1%
Napthalin roth.	45	1,000,000	1	39	0.05
Fluorescein.	300	150,000	10	30	0.11
Rhodamin.	360	125,000	20	40	0.14
Cyanin.	170	270,000	40	45	0.52

could be found in any part of the spectrum, although the sensitiveness of the bridge was such that a change of .008 per cent. could have been detected. The solution was an old one and had prob-

ably been made with commercial alcohol, since the resistance, 90,000 ohms, was much lower than that of the other solutions. For this reason we are not inclined to look upon this single experiment with a non-fluorescent solution as possessing much significance.

In the preceding description of the experiments upon fluorescent solutions we have ascribed the observed movements of the galvanometer needle to a change in the *resistance* of the solution. The galvanometer deflections undoubtedly indicate a disturbance in the balance of the bridge; but this disturbance might equally well result from a diminution in the E.M.F. of polarization. Without special modifications the method does not permit a separation of these two possible effects. In the case of eosin special experiments were made bearing upon this point; but with the other solutions we have no direct evidence to show that the observed change is not due to the influence of light upon the polarization of the cell.

The experiments referred to in the case of eosin were of two kinds. In the first of these a bridge method was employed as before. The solution was contained in a glass tube originally about 5 mm. in diameter. A portion of this tube had been drawn down to a diameter of about 1 mm. and the current passed through the liquid contained in this contracted part. The platinum electrodes were placed in the larger part of the tube at each end. We were thus able (1) to illuminate the solution about either electrode while the remainder of the tube remained dark; or, (2) to illuminate the contracted part of the tube while screening the electrodes. In the latter case the effect was observed, as in the experiments already described. In the former case only a very small change could be detected. Although this arrangement was less sensitive than that in which the cell shown in Fig. 28 was used, the results show that only a small part of the effect previously observed can be attributed to a change in polarization.

The other experiments with eosin that bear upon the question of polarization were of an entirely different character, and represent one of our many early attempts to devise a satisfactory method of attacking the general problem. Fig. 29 shows both the form of tube used to contain the solution and a diagram of the connections. The

platinum wire electrodes *a*, *b* were connected to the terminals of the secondary of an induction coil, *I*, and to the two pairs of quadrants of an electrometer, *E*. The electrode *C* at the center of the tube was connected to the needle. The primary of the induction coil was excited by an alternating current of 120 cycles. When the solution was not illuminated the electrometer needle stood nearly at its zero. Under these circumstances illumination of the upper half of the tube produced a deflection in one direction, while the illumination of the lower half gave an approximately equal deflection in the opposite direction. The direction of the deflection in each case was such as to indicate a decrease of resistance. The spectrum of the arc was used in these experiments as in those made by the

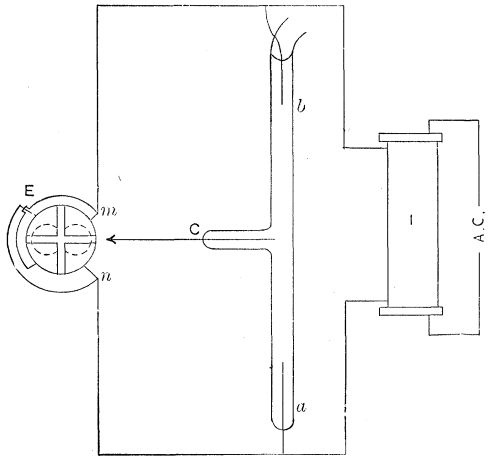

Fig. 29.

bridge method; and the evidence that the effect was due to fluorescence, and not to rise of temperature, was as conclusive as in the experiments already described. The method was less sensitive, however, and was therefore used only in the case of eosin.

The results of these two widely different methods are conclusive in showing that in the case of eosin we have to deal with a change in conductivity rather than a change in polarization. That this statement is equally true in the case of the other solutions tested appears probable.