STUDIES IN LUMINESCENCE.

By Edward L. Nichols and Ernest Merritt.

VIII. The Influence of the Red and Infra-red Rays upon the Photoluminescence of Sidot Blende.

THE effect of the red and infra-red rays in suppressing the phosphorescence of various substances has long been known,[1] and has frequently been utilized in the study of the infra-red spectrum. The effect is exhibited by Sidot blende more strongly perhaps than by any of the other phosphorescent sulphides. In the preceding paper of this series[2] we have called attention to another effect produced by the longer waves, namely the restoration of a screen of Sidot blende, after the excitation and complete decay of phosphorescence, to a standard condition, so that the result of a subsequent excitation shall be unaffected by the previous history of the substance. While this new effect is doubtless connected in some way with that first mentioned, the nature of the relationship between the two is by no means clear. For this reason, and because of the bearing of the phenomena upon the general theory of luminescence, we have investigated the influence of the longer waves upon the luminescence of Sidot blende under a variety of different conditions. The experiments to be described in the present paper were made during the progress of work upon the luminescence of Sidot blende that has already been published, and have extended over a period of about three years. While there are certain parts of the work where additional investigation is much to be desired, it has seemed inadvisable to postpone longer the publication of the results thus far obtained, since the experimental work has been interrupted and cannot be taken up again for some months.

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[1] References to the literature of the subject are given by Dahms, Annalen der Physik, Vol 13, p. 425.

[2] Further Experiments on the Decay of Phosphorescence, Physical Review, Vol. 23, p. 37, 1906.

The work naturally falls under several heads as follows:

1. The effect upon the luminescence of Sidot blende of exposure to the longer waves *before* excitation.

2. The effect of the longer waves *during* excitation.

3. The effect of the longer waves *after* excitation, *i. e.*, during the decay of phosphorescence.

4. The influence upon the effect studied of the wave-length of the red and infra-red rays used.

1. The Effect of the Longer Waves Before Excitation.

Experiments described in the preceding paper of this series have shown that when Sidot blende is excited to luminescence "some change is produced in the material by the action of the exciting light, and that this change persists for a considerable period after all visible phosphoresence has ceased. In other words the effect of a given excitation in producing phosphorescence depends upon the previous history of the phosphorescent substance. If the screen is allowed to rest in the dark for a number of hours this semi-perma-

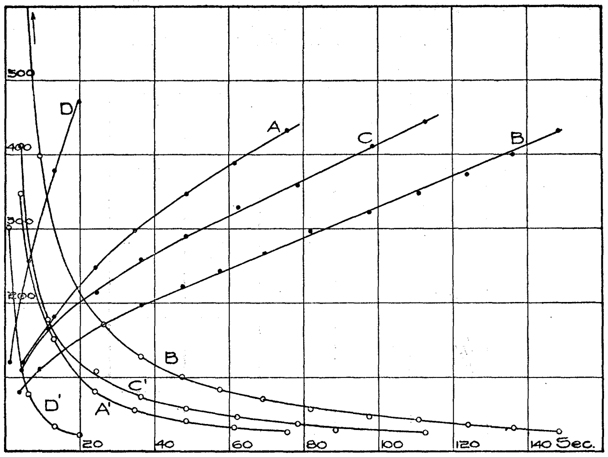

Fig. 42. Illustrating the relative effect of rest and of exposure to infra-red.
A, 10 sec. excitation after rest of 24 hours in the dark.
B, 2 min. excitation.
C, 10 sec. excitation immediately after *B*.
D, 10 sec. excitation after exposure of 4 min. to infra-red from 50 candle power lam p
Curves A', B', C', D' correspond to A, B, C, D except that I is plotted in place of $I^{-\frac{1}{2}}$.

nent effect of exposure in part dies out. But rest alone does not restore the screen completely even if continued for several days." An exposure of a few seconds to the rays from a 50 c.p. lamp seen through ruby glass is however sufficient to restore the screen to what seems to be a definite standard condition.

The phenomenon in question is well illustrated by the curves of Fig. 42, which is reproduced from our last article. If we compare curves *A*, *C* and *D*, all corresponding to the same excitation, it is clear that exposure to the longer waves *before excitation* exerts a very marked influence upon the rate at which the phosphorescence, excited after this exposure, will decay. While the semi-permanent change produced by excitation is partly lost as the result of prolonged rest in the dark, rest alone is not a very satisfactory means of restoring the substance to a standard condition. Thus a rest of 24 hours brings about a change in the decay curve following a 10-sec. excitation from *C* to *A*. Rest for several days would shift the curve somewhat further to the left. But even a rest of several weeks failed to bring the decay curve as far to the left as curve *D*.

Curve *D*, Fig. 42, was taken after an exposure of four minutes to the longer waves. A very much shorter exposure would have been

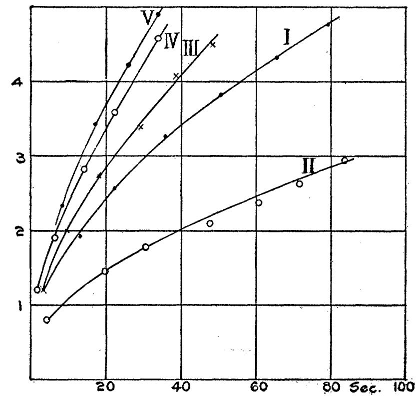

Fig. 55. Effect on the decay curve of exposure to the infra-red for different times.
Curve I. 10 sec. exposure after 48 hrs. rest in the dark.
Curve II. 2 min. exposure.
Curve III. 10 sec. exposure after 1 sec. infra-red.
Curve IV. 10 sec. exposure after 3 sec. infra-red.
Curve V. 10 sec. exposure after 60 sec. infra-red.

nearly, if not quite, as effective. This point is brought out by the curves of Fig. 55, which were taken to determine the way in which the effect depended upon the duration of exposure to the longer waves. In taking these curves the procedure was as follows: In each case the screen was first exposed for two minutes to the mercury arc; the phosphorescence was then allowed to decay for two minutes, at the end of which time, while still visible, it was too faint for measurement. The screen was then exposed to the rays of a 50 c.p. lamp at a distance of 5 inches, a piece of ruby glass being interposed between the lamp and the screen; the duration of this exposure was 1 sec. for Curve III., 3 sec. for Curve IV., and 60 sec. for Curve V. After this exposure to the longer waves the screen was excited by the mercury arc for 10 sec., and the decay curves shown in Fig. 55 were observed by the procedure described in our last paper.

It will be observed that even an exposure of only 1 sec. is more effective than 48 hours' rest. It will be noticed also that 3 sec. exposure to the longer waves is nearly as effective as an exposure of a minute.

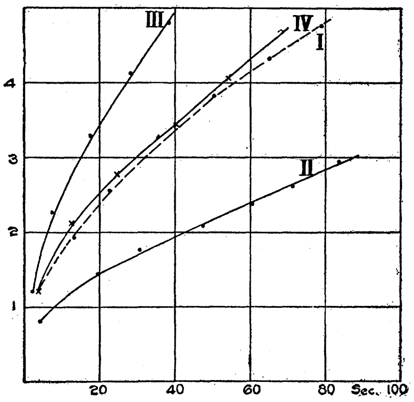

Fig. 56. Effect on the decay curve of exposure to the infra-red for different times. The intensity of the infra-red rays was here only about $\frac{1}{36}$ of the intensity used for the curves of Fig. 55.

Curve I. 10 sec. exposure after 48 hrs. rest in the dark.
Curve II. 2 min. exposure.
Curve III. 10 sec. exposure after 60 sec. infra-red.
Curve IV. 10 sec. exposure after 15 sec. infra-red.

With red and infra-red rays of less intensity a longer time is required to destroy the effect of previous excitation. The curves of

Fig. 56 were taken with a procedure similar to that for Fig. 55, except that the distance of the 50 c.p. lamp from the Sidot blende screen was 30 inches instead of 5 inches. Exposure for 60 seconds to these less intense rays produces as great an effect as a similar exposure to the stronger rays. But this is not true for shorter exposures. While the ultimate effect of the weaker rays is apparently the same, more time is required to produce the change when the rays are of small intensity; approximately, at least, the change produced depends upon the product of intensity and duration of exposure.

The experimental data bearing upon this phase of the subject are so meager as to permit of only the most general conclusions, and additional experiments are much to be desired. So far as they go however the results indicate that the condition in which the material is left after the excitation and decay of phosphorescence is an unstable one, due perhaps to some new grouping of the molecules of the phosphorescent material. During rest in the dark accidental disturbances of various kinds may cause the substance to return more or less completely to its normal condition. The effect of rest is therefore uncertain, depending as it does upon the extent to which various obscure and perhaps unrecognized agencies are active. Certain waves, however, lying chiefly in the infra-red region of the spectrum, have a definite and positive effect in restoring the substance to its normal condition.

Influence of the Longer Waves During Excitation.

We have seen that a condition is developed in Sidot blende by excitation which is favorable to the production of strong luminescence by a subsequent excitation. A long excitation is therefore more effective than exposure to equally intense exciting rays for a shorter period; for the favorable condition developed in the early stages of excitation makes the exciting rays that act later more effective. The luminescence of such a substance during excitation — *i. e.*, the fluorescence — will be relatively weak when excitation first begins and will increase in intensity as the exposure continues, reaching a steady value only after a considerable time. In Sidot blende, with the exciting light used in most of our experiments, three or four minutes were required to reach a steady value.[1]

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[1] See the preceding paper of this series, *l. c.*

The steady condition finally reached is manifestly characterized by equality in the rates of development and decay of the condition favorable to luminescence to which we have just referred. If we think of this favorable condition as being due to some new grouping of the molecules, then the condition of steady fluorescence is reached when these favorable groups are being broken up, either spontaneously or through the action of some outside agent, just as rapidly as they are formed by the action of the exciting light.

It is clear that the intensity of steady fluorescence will be made less by any agent which increases the rate at which the assumed favorable grouping is destroyed. Now it is precisely this effect that is exerted by the red and infra-red rays; and we should therefore anticipate that the fluorescence of Sidot blende would be diminished by the action of the longer rays.

This effect of the longer waves, which does not appear to have attracted much attention heretofore, may readily be made very marked indeed. Thus the rays from a projecting lantern after passing through a sheet of hard rubber 0.2 mm. thick are able to reduce the fluorescence of Sidot blende so greatly as to leave the intensity only a few per cent. of its normal value, and this too with very intense excitation. If the ultra-violet rays of a spark are used for excitation numerous lecture experiments may be devised for demonstrating the existence of the invisible rays at the two ends of the spectrum. As compared with the experiments first proposed by Dahms, in which the effect of the infra-red rays upon phosphorescence is utilized, this procedure has the advantage of giving a persistent rather than a fleeting effect.

In studying the influence of the longer rays upon fluorescence we have directed our attention especially to the distribution of the effect throughout the fluorescence spectrum. While the result of exposure to longer waves is to unquestionably diminish greatly the *total* brightness of the fluorescence light, it might be that in certain restricted regions of the spectrum the intensity would be increased rather than diminished, or at least that the effect of the infra-red rays would vary greatly in magnitude in different parts of the fluorescence spectrum.

For the work on this phase of the subject the Sidot blende screen was mounted in front of a Lummer-Brodhun spectrophotometer, with an acetylene flame as a comparison source as in our previous work. The infra-red rays from an arc fell upon the screen after passing through hard rubber. The intensity of fluorescence was then measured in different parts of the spectrum, first with, and then without the action of the longer waves, the excitation remaining constant. As exciting source a mercury vapor lamp was first used, the lamp being made of the so called "Uviol" glass, which possesses an unusual transparency to the ultra-violet rays.

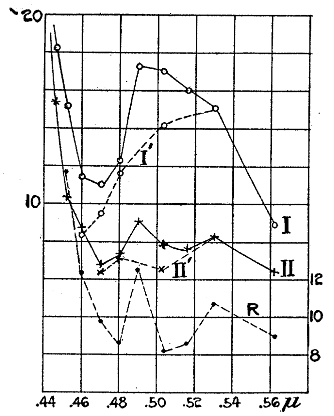

Fig. 57. Effect of infra-red on fluorescence. Sidot blend excited by "uviol" mercury vapor lamp.

Curve I. Fluorescence spectrum.

Curve II. Fluorescence spectrum when the screen is exposed to infra-red during excitation.

Curve I.′ Fluorescence spectrum with plate glass between screen and mercury lamp.

Curve II.′ Same as I.′ except that screen is also exposed to infra-red.

Curve *R*. Reflection of exciting light from white surface.

In Fig. 57, Curve I. shows the ordinary fluorescence spectrum of Sidot blende produced by the mercury lamp, while Curve II. shows the spectrum as modified by exposure to the infra-red. In the case of Curves I.′ and II.′ a sheet of ordinary glass was interposed between the lamp and the screen, so that the ultra-violet rays were in large part removed from the exciting light. It is clear that the ultra-violet-rays of the Uviol lamp introduce a band at about .49 μ which overlaps and distorts in an annoying way the usual green band at 0.51 μ.

A more annoying source of disturbance in these experiments, however, was the light reflected from the screen, which was mixed with fluorescence light and practically inseparable from it. By making observations only at points lying between the bright lines of the mercury spectrum we had expected to be untroubled by reflected light. But owing either to optical imperfections in the apparatus or to the existence of a faint continuous spectrum in the light from the lamp, there was always enough reflected light in the field of the spectrophotometer to be an important and disturbing factor. To get some idea of the intensity and distribution of this reflected light we made the observations plotted as Curve *R* in Fig. 57 with a screen of MgO on cardboard instead of the Sidot blende screen. To avoid confusion this curve is displaced downward in the plot. The intensity for points on Curve *R* should be read from the right hand side of the figure.

The irregular distribution of the reflected light and the great uncertainty in its measurement make the experiments plotted in Fig. 57 of little quantitative value. Especially is this true for the violet end of the spectrum, where the reflected rays are of great intensity. We could not even feel sure that the longer waves produced any effect at all in this region.

With a different zinc sulphide screen, the so called "Emanations pulver" referred to in the foregoing paper of this series, the conditions were somewhat more favorable. The curves in Fig. 58 show the ordinary fluorescence spectrum (Curve I.); the fluorescence spectrum with exposure to weak infra-red rays (Curve II.); the fluorescence spectrum during exposure to strong infra-red rays (Curve III.); and the reflected light determined as before. Different intensities of infra-red were obtained by using in one case one piece of black rubber and in the other case two pieces between the arc lamp and the screen. By this procedure it is possible to determine the *ratio* of the effects produced by strong and weak infra-red, in spite of the uncertainty in the value of the reflected light. Thus the difference between the ordinate of Curve I. and the corresponding ordinate of Curve II. is a measure of the effect produced by weak infra-red; reflected light, since it affects

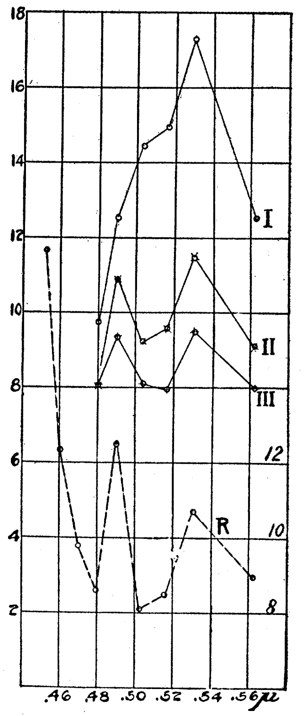

Fig. 58. Effect of infra-red on the fluorescence of "Emanationspulver," excited by the uviol lamp.

both measurements, is eliminated by taking their difference. Similarly the difference between the ordinates of Curves II. and III. measures the effect of the stronger infra-red. It is interesting to note that the ratio of these effects is nearly constant throughout the green band. Beginning at 0.562 μ and running toward the violet the ratio has the values: 1.32, 1.36, 1.31, 1.22, 1.94. Except for the last point, which is so near the edge of the band that the intensity of fluorescence is small, the values are constant to within observational errors. This fact adds another to the many that have been observed in the course of our work on luminescence to indicate that each band in a luminescence spectrum behaves as a unit — that whatever affects one part of the band affects all other parts of the band in the same proportion.

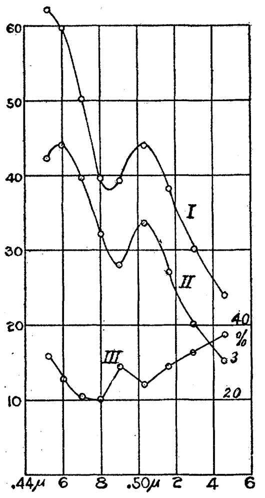

Fig. 59. Effect of infra-red upon the fluorescence of "Emanationspulver" excited by the ultra-violet rays of an iron spark.

In some ways the most satisfactory method of studying the effect in question is to use only ultra-violet light in excitation. All troubles due to reflected light are in this case removed. The results of this procedure in the case of the original Sidot blende screen used in our earlier experiments are shown in Fig. 59. An iron spark was used as an exciting source, a spectrum being formed by a quartz train and only the ultra-violet rays used. The source of infra-red was an arc lantern whose rays passed through a sheet of hard rubber 0.2 mm. thick. The effect of exposure to longer rays during excitation by the ultra-violet rays of the iron spark was to change the fluorescence spectrum from Curve I. to Curve II. The diminution in intensity brought about by exposure to the longer rays, expressed as a fraction of the ordinary fluorescence at the same wave-length, is given in Curve III.

More extended experiments are required to determine whether the change in the effect from 38 per cent. at 0.546 μ to 20 per cent. at .480 μ is real, or the result of errors. It does not seem likely, however, that experimental errors alone can account for so great a change. In interpreting the results we must bear in mind the fact that the spectrum shown in Fig. 59 obviously consists of two overlapping bands, and that the infra-red effect may differ for the two. It is highly probable also that still another band is present at 0.49 μ, as was found to be the case with ultra-violet excitation in the experiments plotted in Fig. 57; and for this band the effect of the longer waves may be different still. It is clear that further experiments on this branch of the subject are needed.

Effect of the Longer Waves During Decay.

In studying the effect of the infra-red rays upon the decay of phosphorescence two methods were used. In the first of these the intensity of the total phosphorescent light was measured by a photometer at different times after excitation had ceased, by the same procedure as that described in our last article. The violet end of the carbon arc spectrum was used for excitation, and a 50 c.p. incandescent lamp as a source of infra-red rays. In these experiments a cell containing a solution of iodine in carbon disulphide was used

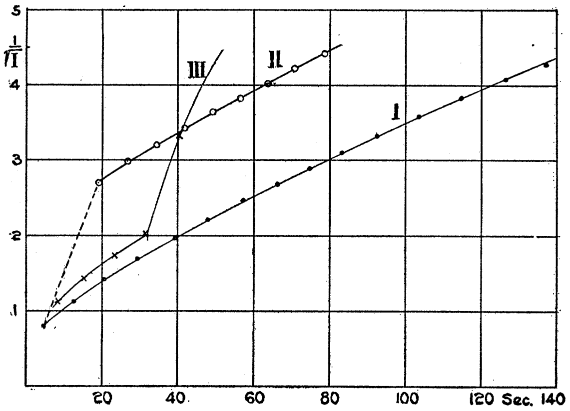

Fig. 60. Influence of exposure to infra-red during decay upon the form of the decay curve.

Curve I. Ordinary decay curve.

Curve II. Screen exposed to infra-red after decay had proceeded for 4 sec. Infra-red cut off at $t = 19$ sec.

Curve III. Screen exposed to infra-red after decay had proceeded for 32 sec.

instead of hard rubber to remove the visible rays. The distance of the lamp from the Sidot blende screen was about 60 cm.

The curves of Figs. 60 and 61 show some of the results obtained by this procedure. In Fig. 60, Curve I. is the ordinary decay curve without exposure to infra-red. In the case of Curve III. the infra-red rays were allowed to fall on the screen when the decay had proceeded for about 32 sec. In Curve II. the infra-red rays were turned on about 4 sec. after the end of excitation and were cut off again at the end of about 19 sec. The great increase in the rapidity of decay brought about by infra-red rays, even when of such small intensity as those used in these experiments, is clearly shown.

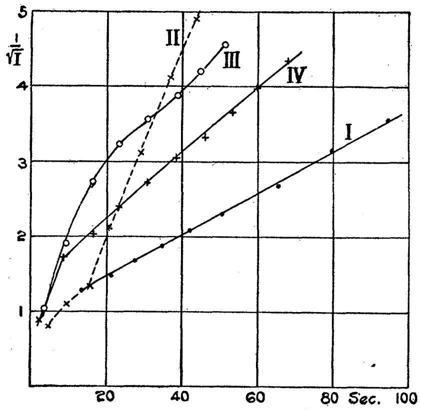

Fig. 61. Influence of exposure to infra-red during decay upon the form of the decay curve.

Curve I. Ordinary decay curve.

Curve II. Screen exposed to infra-red after the decay had proceeded for 18 sec.

Curve III. Screen exposed to infra-red during excitation and for the first 16 sec. of decay.

Curve IV. Screen exposed to infra-red during excitation and for the first 9 sec. of decay.

There was no indication in these experiments of any temporary *increase* in the brightness of phosphorescence when the rays were first turned on, as has been noted by many observers in the case of Balmain's paint and other phosphorescent sulphides. Dahms has already called attention to this peculiarity of Sidot blende. The effect of the longer waves in suppressing phosphorescence has sometimes been explained by assuming that these rays act in the same way as does a rise of temperature; *i. e.*, that they accelerate the process which causes phosphorescence, so as to produce a brief flash, due to the sudden liberation of the energy stored during excitation, followed by a complete loss of luminescence when the stored energy has been used up. While this explanation of the phenomenon may be correct for the other phosphorescent substances it cannot be applied without essential modification to the case of Sidot blende.

Perhaps the most striking feature of the curves in Fig. 60 is the nearly exact parallelism that exists between the later part of Curve III. (after the infra-red rays were cut off) and the straight part of the ordinary decay curve. The action of the longer waves appears to be to bring the material quickly into the same condition as regards ability to emit light that it would have acquired at the end of a much longer period of ordinary decay.

In the case of Curves III. and IV. of Fig. 61 the screen was exposed to infra-red during excitation and during the early stages of decay. The infra-red rays were cut off at the points indicated by the break in the curves. It will be noticed that the latter portion of Curve III. is nearly parallel to the straight part of the ordinary decay curve; but in Curve IV., where the infra-red was cut off earlier, the straight part of the curve is not even approximately parallel to Curve I.

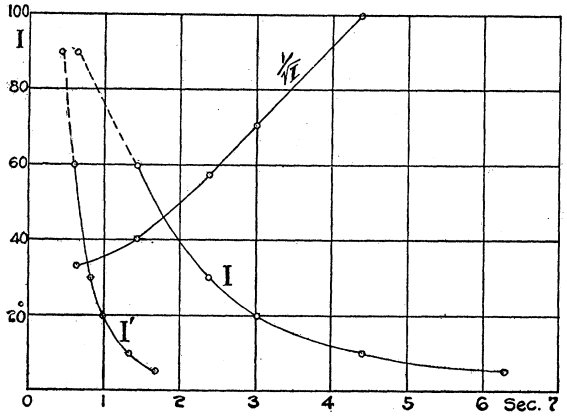

Fig. 62. Influence of exposure to infra-red on form of decay curve.
Curve I. Ordinary decay curve for $\lambda \times 0.497\ \mu$.
Curve II. Screen exposed to infra-red immediately after the end of excitation.

For the early stages of decay a number of curves were taken by means of the spectrophotometer, the method being that described in the fifth and sixth papers of this series.[1] With this method it is impracticable to follow the decay for more than a few seconds, since the illumination of the spectrophotometer field soon becomes too faint for accurate measurements. The method possesses a great advantage, however, in the fact that the effect of the long waves can be determined for different parts of the phosphorescence spectrum.

For the curves shown in Figs. 62 and 63 the exciting light was the violet of the carbon arc spectrum. For the curves of Figs. 64–67 a spark between cadmium terminals was used in excitation. The intensity of phosphorescence has been plotted in all of these curves instead of the reciprocal square root, although in some cases the latter value has been plotted also. In all these figures the curve marked I. was taken without infra-red[2] and that marked I.′ with infra-red. In general the exposure to infra-red began at the instant the excitation ceased, the shutter being arranged so that the same movement that cut off the exciting rays allowed the infra-red rays to fall upon

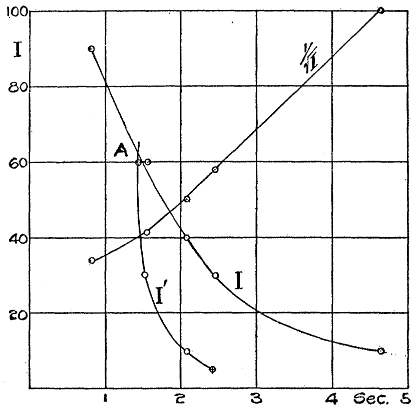

Fig. 63. Curve I. Ordinary decay curve for $\lambda \times 0.497 \mu$.
Curve II. Screen exposed to infra-red after decay had proceeded to *A*.

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[1] Physical Review, Vol. XXI., p. 247; and Vol. XXII., p. 279.

[2] The carbon arc was used as a source of infra-red, a piece of dense ruby glass serving as a filter. Red light, and perhaps a little yellow light, was therefore present in addition to the infra-red. There has been nothing in our experiments to indicate that the presence of these visible rays modifies the results in any way.

the screen. In the case of Fig. 63 exposure to the infra-red did not begin until about 1.4 sec. after the end of excitation. Numerous curves of this kind were taken in which the exposure to infra-red began at different times after the beginning of decay. All of these curves show the same sudden drop in intensity at the instant that the long waves begin to act.

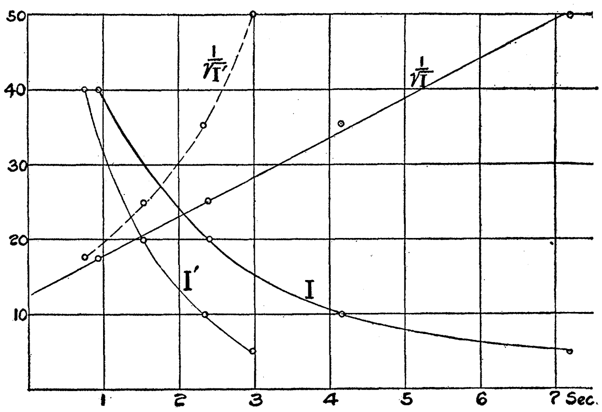

Fig. 64. Decay curves with and without infra-red. $\lambda = 0.546\mu$.

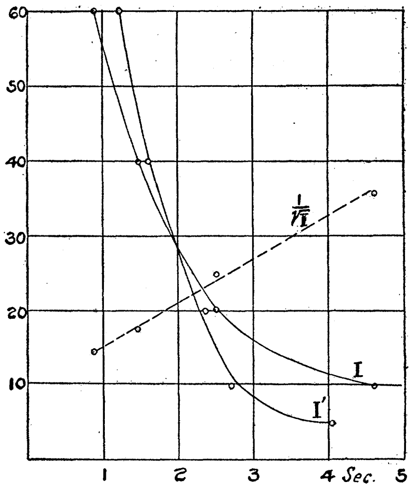

Fig. 65. Decay curves with and without infra-red. $\lambda = 0.474\mu$.

The curves of Figs. 62, 63, and 64, except for the method of plotting, are quite similar to the curves for the total light obtained by the photometer method first described. Apparently the action of the longer waves during the first few seconds of decay is quite similar to its action later. It will be observed that the curves of Figs. 62–64 refer to regions of the phosphorescence spectrum either near the maximum or toward the red edge of the band.

Figs. 65, 66 and 67 show the influence of the longer waves upon those regions of the fluorescence spectrum lying near and beyond the violet edge of the green band. Here the effect seems to be entirely different. At 0.445 μ (Fig. 67) the effect of exposure to infra-red is to retard the decay of phosphorescence instead of to accelerate it. In the region lying between the green band (0.51 μ) and the violet band (0.45 μ) the effect of the infra-red is at first to retard the decay and later to accelerate it (Figs. 65 and 66).

Owing to the faintness of the spectrophotometer field and the rapidity with which the phosphorescence decays it is difficult to determine the form of the curves in the early stages of decay with accuracy. Especially is this true in the blue and violet, owing to the small luminosity of this region of the spectrum. Each point plotted represents however the average of a number of separate readings. For each pair of points the observations for the time of decay with and without infra-red were taken alternately. No special precautions were taken to keep the exciting source constant. The slight initial curvature of the line for $I^{-\frac{1}{2}}$ in Figs. 62 and 63, where the exciting light was from the carbon arc is perhaps to be explained as the result of variations in this source. In the case of the other observations, in which a spark was used in excitation, the points for $I^{-\frac{1}{2}}$ lie reasonably well upon a straight line, and thus give a check upon the accuracy of the observations.

The remarkable reversal in the effect of infra-red in passing through the luminescence spectrum received ample qualitative confirmation. With the spectrophotometer set for some region in the blue or violet the brightness of the field increased noticeably for a few seconds when the screen was exposed to infra-red during decay, even when the exposure first began several seconds after the end of excitation. The same effect was observed in the case of "emanations pulver" and Balmain's paint. In the case of the latter substance the flash that accompanied exposure to the longer waves developed more slowly and lasted longer than in the case of Sidot blende.

Two interpretations of the results brought out in Figs. 62–67 suggest themselves. Neither, however, is wholly satisfactory.

In all of these experiments the luminescence spectrum consisted of two bands, namely, the green band at 0.51 μ, and the violet band at about 0.45 μ. It is possible that the infra-red rays retard the decay of phosphorescence in the case of the violet band and accelerate it in the case of the green band. In the curves of Fig. 67 we are dealing with the violet band only; in Figs. 62, 63 and 64 the light is almost entirely from the green band; but at wave-lengths 0.474 μ (Fig. 65) and 0.464 μ (Fig. 66) the light entering the collimator slit must be partly from one of these bands and partly from the other. The violet band apparently decays more rapidly than the green band. (Compare the slant of the line for $I^{-\frac{1}{2}}$ in Fig. 67 and Fig. 64.) If the violet band is initially the brighter of the two the retarding effect of the infra-red upon the decay of this band will predominate in the early stages of decay; while later, when the violet band has nearly died out and the light is chiefly due to the green band, the opposite effect will predominate. The two curves I. and I.′ will therefore intersect, as shown in Fig. 65 and Fig. 66.

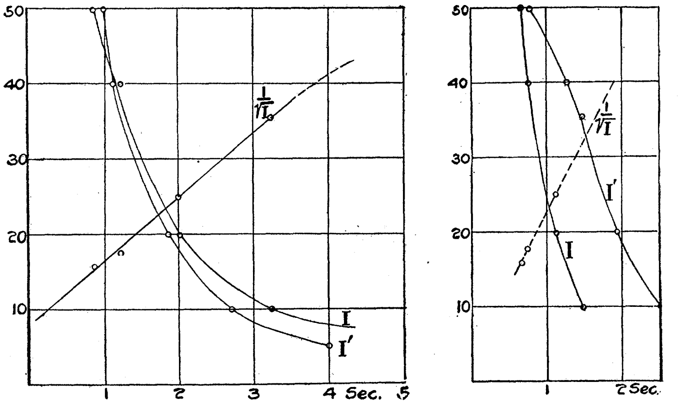

Fig. 66. Fig. 67.

Decay curves with and without infra-red. $\lambda = 0.464\mu$ (Fig. 66) and $\lambda = 0.445\mu$ (Fig. 67).

Two objections may be urged to this explanation. If the light in the case of Figs. 65 and 66 is from two bands that decay at different rates we should hardly expect the relation between t and $I^{-\frac{1}{2}}$ to be as simple as the linear relation that holds for the green band alone. Yet the deviation from a linear relation in both these cases is well within the errors of observation. Again, if the infra-red rays increase the brightness of the violet band after excitation has ceased it would seem reasonable to expect a similar effect during excitation. Yet the effect during excitation (Fig. 59) is practically the same for both bands.

We were first led to expect increased brightness in the violet during exposure to the infra-red, and to undertake experiments in the hope of detecting such an effect, as the result of an entirely different line of reasoning. Looking upon phosphorescence as due to the recombination of ions dissociated by the action of the exciting light, we have explained the fact that the phosphorescence light is of greater wave-length than the exciting light (Stokes' Law) briefly as follows: Dissociation results from the violent resonant vibration of a neutral molecule of the active substance under the influence of the exciting waves. The wave-lengths of maximum resonance and therefore maximum excitation is determined by the natural period of vibration of the active molecule, which is influenced to some extent, but not greatly, by the surrounding solvent. The charged ions resulting from excitation will however be attracted by the neutral molecules of the solvent and will form the nuclei of heavy aggregations of molecules; and recombinations of the ions will therefore occur under conditions which make the resulting vibrations longer, on the whole, than the period of the active molecules before dissociation. Hence the well-known displacement of the luminescence spectrum with reference to the absorption spectrum.

Now the effect of the infra-red rays may be to so shake up the molecules of the solvent as to prevent the loading down of the ions by the attraction of neutral molecules, or to destroy such heavy aggregations if already formed. Under the influence of the infra-red therefore the light emitted will be due largely to the vibrations that occur during the recombination of *unloaded* ions and will be of the same wave-length as that which the active substance absorbs.

If the screen is exposed to infra-red rays after excitation we should expect a decrease in the intensity of phosphorescence throughout the phosphorescence band due to the breaking down of the groups of molecules referred to above. But owing to the resulting increase in the number of unloaded ions we should also expect the emission of light whose wave-length is that of the resonant absorption band of the substance. Now the absorption band always lies on the ultra side of the luminescence band, and usually the two bands overlap. (That this is the case with Sidot blende is evidenced by the fact that this is one of the substances for which Stokes' Law, in its strict form, is violated.) Exposure to infra-red should therefore produce increased intensity near and beyond the violet edge of the phosphorescence band ; which is exactly what we have observed.

In the region where the absorption and emission spectra overlap, the effect will be more complicated. While the light in this region due to the ordinary luminescence band will diminish, there will be at the same time a temporarily increased emission due to the recombination of the unloaded ions that are shaken loose by the infra-red vibrations. A bright flash immediately after the exposure to infra-red followed by decay more rapid than the normal, is therefore to be expected in the intermediate region corresponding to Figs. 65 and 66.

The effect of the longer waves during excitation (Fig. 59) is unfortunately as hard to reconcile with this explanation of the phenomena as with that first suggested. It seems on the whole preferable to wait until additional data have been accumulated and other substances studied before attempting to develop the theoretical side of this extremely puzzling subject.

VARIATIONS OF THE EFFECT WITH THE WAVE-LENGTH OF THE LONGER WAVES.

In the case of several phosphorescent substances, including Sidot blende, the effect of rays of different wave-length in suppressing phosphorescence has been studied by a photographic method of Dahms. Our own results, obtained by an entirely different method, in general confirm the conclusions reached by Dahms in a very satisfactory way.

The arrangement of apparatus was similar to that used in our first experiments on the decay of phosphorescence.[1] A spark was used for excitation and a shutter was so arranged that the screen was exposed to the infra-red rays and the phosphoresence light allowed to fall on the slit of the spectrophotometer at the same instant that the excitation was brought to a close by short circuiting the spark. A Nernst glower was used as a source of infra-red rays. This was mounted in the place of the slit of a large mirror spectrometer with quartz prism.[2] The Sidot blende screen was covered with black paper except for a narrow rectangular region having about the same width as the Nernst glower. The adjustment of the spectrometer having been determined by observations in the visible spectrum, wave-lengths in the infra-red were computed from the angle of deviation. The effect of different rays from the Nernst glower was measured by the difference between the times required for the phosphorescence to fall from its initial intensity to a definite

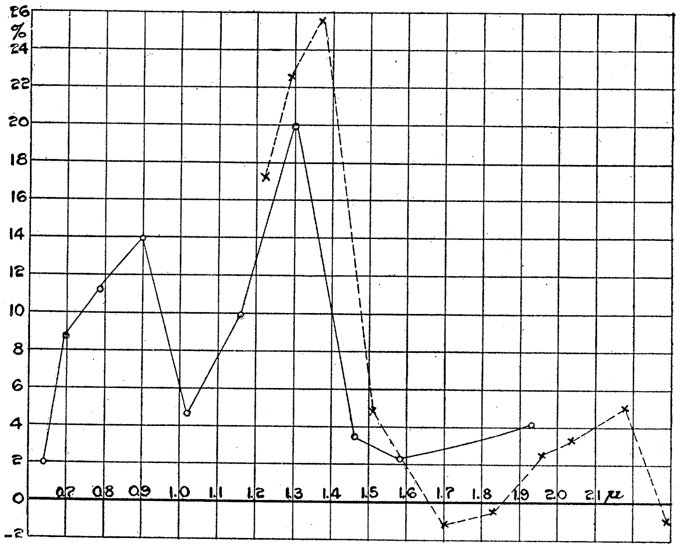

Fig. 68. Effect of infra-red rays of different wave-length. Ordinates represent the percentage diminution in the time of decay under the influence of infra-red.

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[1] PHYSICAL REVIEW, Vol. 21, p. 247, 1905.

[2] Tests (by direct eye observation) with a rock salt prism showed that no effect was observable for wave-lengths longer than those transmitted by quartz.

final intensity with and without exposure to the rays to be tested. Each point on the curves shown in Fig. 68 is determined from the average of ten observations with infra-red and ten without, the observations being made alternately. The difference between the two, expressed as a fraction of the normal time of decay, has been plotted for the different wave-lengths used, which ranged from 0.6 μ to 2.3 μ. The observations refer to the region of maximum intensity in the phosphorescence spectrum (0.512 μ).

Referring to Curve I., Fig. 68, it will be seen that the effect of the longer waves is observable to some extent in the visible region. A maximum is reached at about 0.9 μ, followed by a minimum at about 1.0 μ and another maximum at 1.3 μ. From 1.2 μ on the observations were repeated under slightly different conditions the following day. (Curve II.) In this case the chief maximum appears to lie at 1.37 μ. The results are probably in all cases uncertain to the extent of 2 or 3 per cent., and errors are especially likely to be serious in regions where the effect is small. For this reason we cannot feel certain of the third maximum at 2.18 μ, although the probability is that it really exists. As far as any important effect is concerned, however, our results confirm the conclusion of Dahms that the action does not extend beyond 1.5 μ.

It can scarcely be doubted that absorption of the active rays is necessary before they can produce any effect upon phosphorescence. It seems probable, therefore, that Sidot blende possesses broad absorption bands with maxima not far from 0.9 μ and 1.37 μ. Experiments with other phosphorescent substances having ZnS as their base will be necessary to determine whether the absorption that determines this effect on phosporescence is characteristic of the solvent ZnS or of the dissolved metal causing luminescence. It is interesting to note, however, that in the absorption spectrum of sphalerite (ZnS) Coblentz has found evidence of bands at about 0.9 μ and 1.4 μ. While Coblentz's work does not indicate great absorption at these points it must be remembered that they fall in the most intense region of the spectrum of a Nernst glower, so that the total amount of energy absorbed might be very considerable.