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On the Change of Absorption Produced by Fluorescence

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II. *On the Change of Absorption produced by Fluorescence.*

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Introduction.

About two years ago, in the spring of 1895, in the course of a conversation with Professor J. H. Poynting on the nature of the phenomenon of fluorescence, in the study of which I was at the time beginning to engage, the suggestion was thrown out by him that possibly fluorescent bodies absorb differently, according as they are fluorescing or not, the rays which they give out whilst fluorescing, thus that a body A would absorb differently, according as it is fluorescing or not, the rays from a similar body B in a state of fluorescence. Some fluorescent bodies undoubtedly do, others do not, absorb, except to a very small extent, the rays which they emit. A *strong* solution of fluorescin or eosin, for instance, hardly permits its fluorescent light to penetrate even a very small thickness. Glass coloured with oxide of uranium is much more transparent, but sulphate of quinine hardly absorbs these rays at all.

The question was whether during the act of fluorescing any change is produced in the nature of the absorption itself, that is, whether during fluorescence there is an increase or diminution of absorption in that part of the spectrum where the emitted rays lie. For instance, with uranium glass the radiation takes place *chiefly* between the D and E lines, so that the absorption power for rays may be different according as the body is examined in the dark or in daylight in this part of the spectrum. Of the five bright bands of which the radiation consists, three lie between the D and E lines, the other two being of less refrangibility and of less intensity in the red and orange (Stokes, 'Phil. Trans.,' 1852).* With the spectroscope I have used I have not been able to see the band in the red, but the

* The series of experiments have been made with uranium glass, as the compounds of uranium exhibit many peculiarities which other bodies do not appear to possess when fluorescing. For instance, the bright bands in the fluorescing spectrum of uranium glass seem to be noticeable in uranium compounds alone. It is also remarkable that crystals of nitrate of uranium have the quality as well as the quantity of their fluorescent light altered by depriving them of part of their water of crystallization.

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other four were quite distinct. The spectrum seemed to me to be of the nature of maxima and minima.

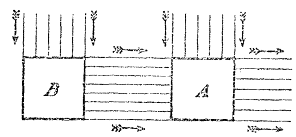
In the summer of 1895 I made some experiments at Trinity College, Dublin, on the electrical conductivity of fluorescent solutions, and endeavoured to determine whether the action of violet or ultra-violet light upon them gave rise to any alteration in their conductivity.

The many difficulties which the experiment entailed prevented me from arriving at any conclusion upon the matter, and I commenced to look for some such effect as Professor POYNTING had suggested.

The experiments have since been carried out in Professor SCHUSTER's laboratory at Owens College.

1. The leading conception in the following paper may briefly be stated thus: Suppose that a body A is transmitting light from a similar body B, which is fluorescing. It is quite conceivable, as Professor POYNTING remarked, that the amount of light from B transmitted by A should be different according as A is fluorescing or not.

Fig. 1.



2. There were some reasons which pointed to the conclusion that something of the sort might happen. It seemed quite possible that the action, if any, of the fluorescent light from B might be to strengthen the fluorescence of the body A when already fluorescing; not that the emitted light would be increased merely by scattering, which would be precisely the same in amount whether the body were fluorescing or not, but that the emission of fluorescent radiation would be increased if light of the same frequency were incident on the radiating body.

The experiments which are described in the sequel do not confirm this supposition, but they prove that the amount of fluorescent light apparently transmitted is very different according as the body through which it passes is fluorescing or not, the amount being very much less, only about one-half (0·57), when fluorescence is taking place than when the body is unacted upon by exciting light.

3. It seemed possible that this effect might be due, *indirectly* at least, to an increased absorption of the incident fluorescent light, if it possessed the property of destroying the fluorescence of the body through which it passed. BECQUEREL has shown that certain infra-red rays have the power of destroying phosphorescence in a substance which is exposed to the phosphorescence-exciting rays. It was therefore possible that the result obtained by me was an effect of this kind, but I think that the experiment described on p. 92 sufficiently proves that, though such an explanation would involve an increased absorption of the annulling rays in order that they might be capable of destroying the fluorescence, the effect I have observed is really not essentially of this kind, but is rather due to an increased direct absorption.

It may be useful if, before entering into an account of the experiments, I give, as briefly as clearness will permit, a short account of the general principles on which the coefficients of absorption may be calculated.

(a) Mode of Determining Absorption.

Let us consider two cubes of the same fluorescent substance (fig. 1).

We shall, by comparing the light from B when fluorescing, which is transmitted by A according as the latter is fluorescing or not, obtain

$$E_1 = E_0 (1 + \alpha),$$
$$E_2 = E_0 \beta,$$

E_0 being the intensity of the light emitted by each cube separately and independently of any light transmitted from the other.

The quantities α and β are clearly the fractions of the incident light transmitted by A according as it is or is not fluorescing. They may be called the coefficients of transmission of the cube under these different circumstances.

Similarly, if we denote the coefficients of absorption of the cube by a and b, and that of reflection at the two faces by r, we have

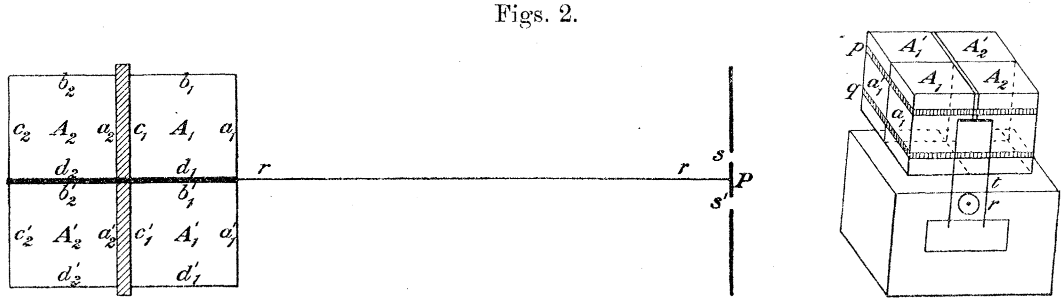
$$\alpha = 1 - (r + a)\,; \qquad \beta = 1 - (r + b).$$

Hence

$$E_1 = E_0 [2 - (r + a)]\,;$$
$$E_2 = E_0 [1 - (r + b)].$$

It has been found more convenient to have to deal with the transmission coefficients rather than with those of absorption, equality in the former of course implying equality in the latter, though, as we have seen, the converse is not necessarily true.

Figs. 2.



Let fig. 2 represent a plan of the plane horizontal surfaces of four similar and equal cubical blocks—A_1, A_2, A'_1, A'_2—of some fluorescent substance such as uranium glass, which is singly refracting. We shall put aside for the present all minor details. Let P be a photometer furnished with two vertical slits, the breadths of which can be varied, and rr a screen, whose plane is perpendicular to that of the paper, serving to

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prevent any light from the vertical surfaces of the cubes A_1 and A'_1 from entering the slits s' and s respectively. We shall suppose that the cubes are illuminated by vertical rays incident perpendicularly to the surfaces A_1, A_2, A'_1, A'_2, *i.e.*, to the plane of the paper. By means of this arrangement we can compare the intensities of the two beams of light coming respectively from the vertical surfaces of the cubes A_1 and A'_1, opposite to the slits s, s'. None of the light from A_1 and A_2 is permitted to pass sideways into A'_1 and A'_2, the two sets of blocks being separated by a screen of black paper. On the other hand, the blocks A_1 and A'_1 are separated from A_2 and A'_2 by a sheet of lead glass, which is very opaque to the fluorescence-exciting rays, so that radiation scattered by A_2 and A'_2 cannot be the source of any part of the fluorescence of A_1 and A'_1, and *vice versâ*. The fluorescence of each block is thus altogether caused by the rays incident perpendicularly to the plane of the paper. If all is right the fluorescent light emitted horizontally from the surfaces a_1 and a'_1 ought to appear the same, and this is tested by the photometer.

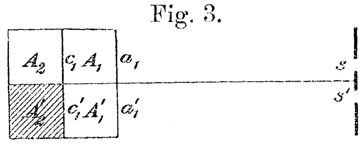
When this condition is fulfilled three experiments are performed: firstly, to determine the coefficient of transmission of A_1 or A'_1 when fluorescing for those rays which the cube itself gives out by fluorescence; secondly, to measure its coefficient of absorption when not fluorescing; and thirdly, to determine independently the ratio of the coefficients, and to compare the value so obtained with that given by the other two results. The last experiment thus serves to verify the first two measurements.

The (α) *Set of Experiments.*

We may call the experiments made to determine the coefficient of transmission during fluorescence the (α) set, and similarly the other two the (β) and $\beta/(1 + \alpha)$ sets, in all of which a proper combination of the cubes A_1, A'_1, A_2, A'_2, is chosen, and the fluorescence-exciting light is allowed to fall upon them, whilst the remaining cube or cubes are screened from its action.

Thus, if we wish to determine the transmission during fluorescence of the block A_1, we screen A'_2 from the incident rays as in fig. 3, these, it must be remembered, are perpendicular to A_1, A'_1, A_2, A'_2, that is to the plane of the paper; hence the light emitted by the surface a_1 will be that due to two cubes, and that from a'_1 to one only. We can compare relative intensities of these by adjusting the slits s, s'. The block A'_2 is not removed, as some of the rays emerging from c_1 towards A_2 are reflected back, and these are compensated by a similar reflection from A'_2. There is no reason to suppose that the reflection would be different according as the reflecting surface is fluorescing or not, because fluorescence is not confined to the surface

Fig. 3.



A portion of the light emitted by A_2 is reflected by the double air layers separating A_2 from A_1, but this is included in the coefficient of reflection r. The light emitted by the surface a_1 is then made up of two parts, *i.e.*, the fluorescent light of A_1 and the fluorescent light of A_2 transmitted by A_1.

Hence the intensity of the light given out by a_1 is $E_0(1 + \alpha)$. The light from A'_1 consists of its fluorescent light only, the internal reflection being the same as in the other two blocks, and is thus $= E_0$.

Denoting the widths of the slits by s and s', and remembering that these quantities are inversely proportional to the intensities, we obtain the equation $1 + \alpha = s'/s$, from which α may be determined.

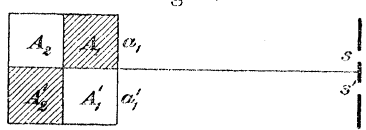
In order to avoid errors arising from want of symmetry, the process is reversed by screening A_2 instead of A'_2, and similarly α is given by the equation $1 + \alpha = \sigma/\sigma'$, σ and σ' being now the widths of the slits s, s'. If there are n observations with the screen in each of these two positions,

$$\alpha = \frac{1}{2n}\left[\Sigma\left(\frac{s'}{s} + \frac{\sigma}{\sigma'}\right)\right] - 1.$$

The (β) *Set of Experiments.*

To determine β for A_1, we screen A_1 and A'_2 from the incident light, as in fig. 4. We can then compare the fraction of the light emitted by A_2 which is transmitted by A_1 (when the latter is not fluorescing) with that emitted by A'_1, which is the same as that from A_2; the constant of reflection being of course involved, as in the previous case.

Fig. 4.



The light coming from a'_1 is then

$$= E_0,$$

whilst that from a_1

$$= E_0\beta.$$

Hence

$$\beta = s'/s.$$

If the process be reversed,

$$\beta = \sigma/\sigma',$$

and after n such observations

$$\beta = \frac{1}{2n}\left[\Sigma\left(\frac{s'}{s} + \frac{\sigma}{\sigma'}\right)\right].$$

The removal of A'_2 is found to make no appreciable difference. The cube A_1 and the glass screen may be moved before the determination is made, to make sure that A_2 and A'_1 radiate equally.

The $\beta/(1 + \alpha)$ *Set of Experiments.*

The ratio $\beta/(1 + \alpha)$ can be obtained independently by the arrangement shown in fig. 5.

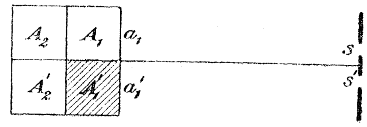
It is easy to see, as before, that if A'_1 be screened, the light coming from a_1

$$= E_0 (1 + \alpha),$$

whereas that from a'_1

$$= E_0\beta.$$

Fig. 5.



Hence

$$\beta/(1 + \alpha) = s/s',$$

and reversing,

$$= \sigma'/\sigma,$$

so that

$$\frac{\beta}{1+\alpha} = \frac{1}{2n}\left[\Sigma\left(\frac{s}{s'} + \frac{\sigma'}{\sigma}\right)\right].$$

This description of the general method will suffice for the present, and the account of the general methods of carrying out an experiment will be found on p. 96.

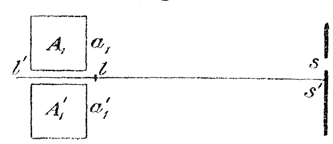
To Determine the Alteration in the Fluorescence on the Supposition that the Fluorescent Light is Capable of Destroying Itself.

Let us suppose that the intensity of the fluorescent light given out by each of two cubes of uranium glass when not exposed to the radiation from each other—that is, when there is an opaque non-reflecting screen (ll, fig. 6) separating them—is equal to E_0, and that when this screen is removed the intensity is equal to E'_0. The blocks are supposed to be illuminated by rays perpendicular to the plane of the paper, and the radiation, the intensity of which is under investigation, to be in the direction perpendicular to the surfaces, a_1, a'_1, of the cubes. The method employed for comparing E_0 and E'_0 depends upon obtaining two photographs on one plate, for comparison side by side.

We proceed thus :—

Let the slit s' be completely closed. Three experiments are made :—

Fig. 6.



1. The light coming from a_1 is photographed when the cube A'_1 is not fluorescing, or the screen ll' interposed. We thus obtain the effect due to E_0.

2. Both cubes are then made to fluoresce, and the screen is removed, in which case we get the effect due to E'_0.

It can thus be found by adjusting the slit s when the photographic effects of E_0 and E'_0 are the same, from which the ratio of the two is determined. As the result of these experiments we are not justified in saying that any material difference between E_0 and E'_0 exists other than that possibly due to scattering.

3. The amount of scattering from A'_1 into A_1, or rather the amount of the A'_1 light scattered by A_1 in the direction outwards from a_1, may be found by making A'_1 fluoresce alone, and noting the effect of the light then falling on the slit s. The

difference due to scattering did not appear to be more than 1 part in 8 at the maximum, and was for the purpose of these experiments altogether inappreciable.

Description of Apparatus.

1. *Fluorescent Cubes.*
2. *Photometer.*

1. The blocks employed are each 1 centim. cube, and are kept together by two indiarubber bands. The two front cubes, A_1, A'_1 (fig. 2), are separated from the two back ones, A_2, A'_2, as has already been pointed out on p. 89, by a plate of glass of thickness (about 2 millims.) sufficient to stop the fluorescence-*exciting* rays scattered by one pair of cubes from entering the other, whilst the cubes A_1 and A_2 are divided by a black paper screen from A'_1 and A'_2, so that no light could pass sideways from A_1 or A_2 to A'_1 or A'_2.

The horizontal surfaces A_1, A_2, A'_1, A'_2, are those which are illuminated, whilst the light studied is that emitted by the surfaces a_1, a'_1.

The surfaces b_1, d_1; b'_1, d'_1; b_2, c_2, d_2; b'_2, c'_2, d'_2, as well as the lower horizontal surfaces parallel to A_1, A'_1; A_2, A'_2, are roughened, so that there is no regular reflection from them, and thus are more or less opaque. But the surfaces a_1, c_1; a'_1, c'_1; a_2, a'_2, are perfectly transparent, as also the upper horizontal surfaces A_1, A'_1; A_2, A'_2.

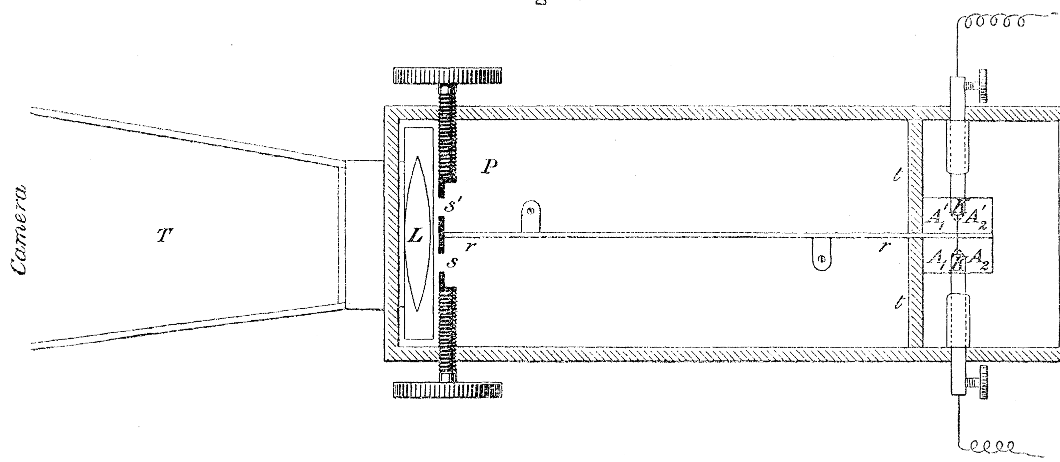
When A_1, A'_1, A_2, A'_2, are all uniformly illuminated by violet or ultra-violet rays, the fluorescence of each block ought to be the same, if we disregard the very refined correction that the blocks A_1, A'_1, have each two transparent vertical surfaces, namely a_1, c_1, and a'_1, c'_1, whereas the blocks A_2 and A'_2 have each only one, a_2 and a'_2. At any rate, since the rays enter vertically, and therefore parallel to these surfaces, any difference that may possibly arise in this way in the intensity of the scattered rays would for all practical purposes be quite immaterial.

We have seen (p. 92) that the error, when sought for, was found to be quite inappreciable and lies within the much larger errors of observation. Apart altogether from this consideration, the fluorescent light emitted horizontally from the surfaces a_1, a'_1, ought to appear the same, if all is right, and this is ascertained by the photometer before an experiment is made.

2. Fig. 7 is a plan of the apparatus showing the position of the fluorescent cubes, &c., in the photographic experiments. The cubes are placed A_1, &c., and are illuminated by light incident vertically upon them either from the spark in air between cadmium electrodes or the electric arc. The source of illumination was almost invariably the former in the photographic determination, the poles being about 15 millims. apart, and 2 centims. above the fluorescent surface. The spark was obtained by the discharge of a Leyden jar charged by the terminals of the secondary of a 10-inch Apps coil.

The photometer, fluorescent substance, and source of illumination in the photographic experiments were enclosed in a wooden box, shown in the figure. The photometer was at one end, and the fluorescent substance and illuminating arrangement at the other.

Fig. 7.



KK represent the electrodes, A_1, &c., the fluorescent cubes, and P the photometer, consisting of two vertical slits, *s*, *s'*, and a double convex lens, L; while *tt* is a cardboard vertical screen, with a horizontal slit, 3 millims. wide, placed immediately in front of the vertical surfaces of the cubes (the slit cannot be shown in the figure). This screen admits of being moved up and down, so that the light at various depths below the illuminated surface may be studied. The usual depth of the upper edge of the slit below the horizontal surface of the fluorescent cubes was about 3 millims. Another vertical screen (*rr*), 6 centims. in length, extends along the whole length of the box from the photometer to the other screen, and divides the horizontal slit into two parts, the light from each part being allowed to pass only through the corresponding vertical slit of the photometer.

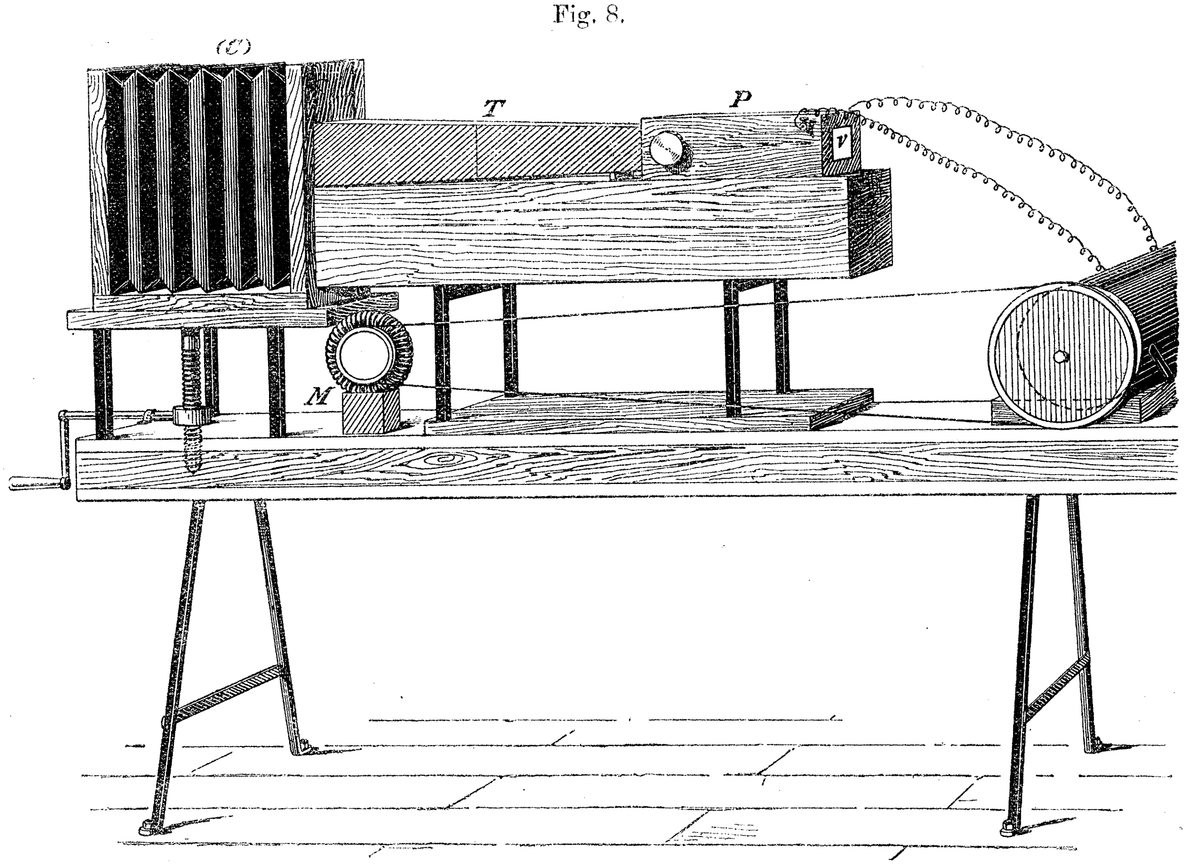
The vertical slits *s* and *s'* were adjustable with micrometer screws.

The lens L (of focal length 4·5 centims.) served to form an image of the horizontal slit in the focal plane of the eyepiece, or on the focussing glass of the camera, which admitted of being raised or lowered, so that, when necessary, a number of photographs could be obtained successively on one plate. The photometer contrivance communicated with the camera by means of the conical tube T, leading up to a front slide which remained fixed whilst the camera itself moved up and down (fig. 8). The distance between the lens L and the focal plane of the eyepiece was 18 centims. The whole of the interior of the apparatus was blackened, so that not the slightest trace of reflection could be perceived.

A screen of blue cobalt glass was interposed between the source of illumination and the fluorescent substance so as to cut off the less refrangible rays. When the apparatus is in use a horizontal green band with a dark vertical line or narrow band in the middle is seen through the eyepiece or on the focussing plate of the camera. The two luminous portions are images of the parts of the surfaces a_1, a'_1, cut off by the horizontal slit immediately in front of them; the screen rr and the paper screen which separates A_1, A_2, from A'_1, A'_2, divide the image of this slit into two parts, and produce the dark vertical line in the middle.

By this arrangement, which was found to be on the whole the most convenient, we have clearly the opportunity, not merely of comparing the two lights side by side, which is absolutely necessary, but also of illuminating the surfaces A_1, &c., by the same source simultaneously and under similar conditions.

Fig. 8.



Any slight amount of light, chiefly blue, but partly red, which, having penetrated the cobalt glass, may have been scattered by the fluorescent substance as *false dispersion* (a term used by STOKES to designate the light scattered by irregular reflection from small particles, which is always polarized in the plane of reflection, and of the same wave-length as the incident light), can be eliminated, in consequence of its being polarized, by interposing a NICOL's prism or a pile of plates between the horizontal and the vertical slits of the photometer. This method is open to the objection that it would weaken the fluorescent light, and it has been thought unnecessary to incur this disadvantage for two reasons. In the first place, the

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whole amount of light scattered has been found to be inappreciable (see p. 93), and on this account alone the portion now under consideration may be neglected. In the second place, if the error were appreciable, it would tend to diminish rather than to increase the apparent difference between the absorptions before and during fluorescence respectively. For the scattered light would add to the total light emitted from a_1, a'_1, and would therefore tend to reduce the effect.

The length of the horizontal slit *tt* being about 2 centims., and its width 2 millims., the image was 6 centims. by 6 millims., for the focal length was 4·5 centims., and the focal distances 6 centims. and 18 centims. respectively. By using a lens of shorter focal length, however, an image of *tt* can be formed on the horizontal slit of a spectroscope placed so that the refraction takes place in a vertical plane, and observations can be made of the absorption in different parts of the spectrum. This, however, is by no means an easy matter to accomplish, and we have confined ourselves to the light taken as a whole.

With reference to the illumination, it was thought at first that one of the electrodes might possibly always be brighter than the other. Accordingly a plan was adopted of continually reversing the current in the primary coil by means of a wheel attached to the commutator of the coil, which was made to rotate by means of a motor. Unfortunately the exposures required in the photographic work were thereby greatly increased. The experiments, however, show that the average illumination obtained from each electrode is, for all purposes with which we are concerned, practically the same.

Eye Observations.

The accuracy of these observations has been found to depend, to a very large extent, upon experience on the part of the observer in dealing with the relative intensity of the lights placed side by side. It is, of course, a familiar fact in photometry that it is very difficult to form a judgment as to the equality of two illuminated surfaces when the illumination is either very feeble or very powerful; and accordingly this is a source of considerable inaccuracy in such determinations. It is not desirable in either case to examine the relative intensity attentively for any length of time, as it is obviously possible, by viewing two feebly illuminated surfaces side by side for a sufficiently long time, to imagine that they are almost equal when really they are not so, and this remark appears to be particularly applicable to such cases in which the two colours are of slightly different tints. Instances have arisen in which it has been impossible to arrive at any result whatever as to the relative intensity. In such cases, however, the difference of tint was conspicuously marked.

It is preferable, when the observations are made by eye, to make a large number of measurements quickly, and to take the means of these first impressions, noting in turn the maximum and minimum widths of the slit, and then reversing the system of screens which serve to shelter the combination of the cubes from the exciting rays.

The screen is so arranged as to admit of being worked by the observer, by means of handles, whilst he is otherwise engaged in taking observations through the eyepiece, but the mechanism by which this is effected is not shown in the figure, which is a sketch of the arrangement adapted chiefly to photographic work. In the eye observation an optical bench was used, being a suitable stand for the apparatus.

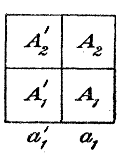
To test the accuracy attained and also the uniformity of the illumination, or rather its symmetry, we may give the result of thirty observations. These observations were made in the earlier stages of the experiments, when but little experience had been acquired. If the illumination had been uniform, the intensity of the fluorescent light should have appeared the same when the slits were of equal width.

Fifteen readings of the left slit, when the right was fixed at 8, give 7·87 as the mean of the readings, the probable error of a single observation being 0·54, and the probable error from the mean 0·135. Similarly the other fifteen observations, when the left slit was fixed at 8 and the right slit movable, gave the mean of the readings of the right slit to be 7·73, the probable error of a single observation being 0·53, and that from the mean 0·133. It may be remarked that in this particular experiment the readings of each observation were taken with an opening slit, and the apparent equality was obtained before the real equality existed, that is that in both sets of observations the mean of the readings was somewhat less than what it should have been; but the process of reversing eliminates this. Then the readings to the two sets of observations are $7·87 \pm 0·135$ and $7·73 \pm 0·133$. The ratio of the illumination of the cubes on the right to that of those on the left is $\frac{7·87}{8}\left(1 \pm \frac{0·135}{7·87}\right)$ in the first set of observations, and $\frac{8}{7·73}\Big/\left(1 \pm \frac{0·133}{7·73}\right)$ in the second, if we neglect the square of $\left(\frac{0·133}{7·73}\right)$.

The ratios of the illumination of the cubes on the right to that of those on the left, as given by the two sets of observations, are $(0·984 \pm 0·017)$ and $(1·035 \pm 0·017)$. The mean of these two ratios is 1·009. The probable error in the ratio is 0·017 in either case. Hence the probable error from the mean, since the two determinations of the ratio of the two illuminations are quite independent, is $\frac{0·017}{\sqrt{2}} = 0·012$. And the probable error of thirty observations is about 1 per cent. from the mean.

In the detection of the change of absorption, an error of 20 per cent. will obliterate the effect.

In tabulating the experiments, the following method has been adopted. The cubes are indicated by the letters A_1, A_2, A'_1, A'_2, the arrangement being as shown in the accompanying figure.



The intensities compared are those of the rays proceeding from the faces a_1 and a'_1.

In each of the experiments one or more of the cubes was shaded from the fluorescence-producing light. The letter in the fifth column indicates which was that protected.

Experiments (α).

Experiment.	No. of observations.	s.	s'.	Shaded cube.	α.	Difference from mean.
I.	20	5·92	4	A_2	0·48	+ 0·03
II.	20	5·45	8	A'_2	0·46	+ 0·01
III.	20	8	5·29	A_2	0·51	+ 0·06
IV.	20	5·89	8	A'_2	0·36	− 0·09
					Mean = 0·45	

Similarly taking in all eighty observations for α, β, and $\beta/(1 + \alpha)$, the following are obtained, the fixed slit being at 8 :—

	Mean of eighty observations of movable slit.	Probable error of a single observation.	Probable error from mean.
(α)	5·52	0·296	0·03
(β)	6·20	0·514	0·05
$\frac{\beta}{(1 + \alpha)}$	4·17	0·50	0·05

Hence

$$1 + \alpha = \frac{8}{5{\cdot}52}\left[1 \pm \frac{0{\cdot}03}{5{\cdot}52}\right]$$
$$= 1{\cdot}449\,[1 \pm 0{\cdot}005]\,;$$

therefore

$$\alpha = 0{\cdot}449 \pm 0{\cdot}005.$$

Also we easily obtain

$$\beta = 0{\cdot}787 \pm 0{\cdot}006$$

and

$$\frac{\beta}{(1 + \alpha)} = 0{\cdot}521 \pm 0{\cdot}006.$$

It may be remarked that the probable error in α is much less than that in β or $\beta/(1 + \alpha)$. My attention was called to this when revising the paper. A glance at figs. 3, 4, and 5 will make this clear. The light emanating from α_1 and α'_1 will be of the same colour in the determination of α; but in the determination of β and $\beta/(1+\alpha)$ we are comparing the light passing through a non-fluorescing body with that emitted by it directly, and the result shows that there is a difference in tint between the light given out by a_1 and that emanating from a'_1.

Substituting the values of α and β thus obtained in $\beta/(1+\alpha)$, we obtain 0·54, which is somewhat larger than that independently determined value 0·52. The difference, though only a third of the probable error of a single observation, is nevertheless three times the probable error from the mean. But this, Professor SCHUSTER suggests, was probably due to slight variations in the symmetry of the illumination. The value of $\beta/(1+\alpha)$ determined independently is, however, quite close enough, and may for all practical purposes be considered a very good verification of the accuracy of the values obtained for α and β.

Taking the observed values of α, β, and $\beta/(1+\alpha)$ to be 0·450, 0·787, and 0·520 respectively, we obtain by the method of least squares* the most probable values of α and β to be $\alpha = 0{\cdot}455$ and $\beta = 0{\cdot}786$, which give $\beta/(1+\alpha) = 0{\cdot}54$ as the most probable value of this ratio.

Hence it appears that the observed values of α and β are more reliable than those of $\beta/(1+\alpha)$.

* Let

$$\alpha_1 = 1+\alpha, \qquad X = \alpha_1 + x,$$
$$\beta_1 = \beta, \qquad Y = \beta_1 + y,$$
$$\gamma_1 = \frac{\beta}{1+\alpha}, \qquad \gamma = \frac{Y}{X},$$

where X and Y are the most probable values of $1+\alpha$ and β. α_1, β_1, and γ being the observed values of $1+\alpha$, β, and $\beta/(1+\alpha)$ respectively.

Then

$$\left(\alpha_1 - X\right)^2 + \left(\beta_1 - Y\right)^2 + \left(\gamma_1 - \frac{Y}{X}\right)^2 = 0,$$

and differentiating, we get

$$\left\{\begin{cases} X^2 + Y^2 - \alpha_1 X - \beta_1 Y = 0\,; \\ Y - \gamma_1 X - X^2(\beta_1 - Y) = 0. \end{cases}\right.$$

Substituting for X and Y their values $(\alpha_1 + x)$ and $(\beta_1 + y)$ and neglecting the powers of x and y higher than the first, we obtain

$$(1)\quad \alpha_1 x + \beta_1 y = 0\,;$$
$$(2)\quad y\,[1 + \alpha_1^2] + \frac{\gamma_1\beta_1}{\alpha_1}\,y - \gamma_1\alpha_1 + \beta_1 = 0.$$

Substituting for α_1, β_1, γ_1, 1·45, 0·787, and 0·52 respectively, we get

$$x = 0{\cdot}005\,;$$
$$y = -0{\cdot}01.$$

Hence

$$X = 1{\cdot}455, \qquad Y = 0{\cdot}786,$$

or the most probable values of α and β are

$$\alpha = 0{\cdot}455\,; \qquad \beta = 0{\cdot}786.$$

The coefficients of absorption a and b are given by the equations (see p. 89)

$$\alpha = 1 - (\gamma + a);$$
$$\beta = 1 - (\gamma + b).$$

Hence

$$r + a = 0{\cdot}545,$$
$$r + b = 0{\cdot}214,$$

and the increase in the absorption, or the difference between a and b, $= 0{\cdot}331$.

INFLUENCE OF TEMPERATURE.

It does not appear that temperature can have any effect on the phenomenon except either by weakening the intensity of the fluorescence of the transmitting cube A_1 or A'_1 by heating effects due to the spark, or by a change of absorption due to temperature directly. But, firstly, since all the fluorescing cubes are uniformly illuminated, and as we are merely concerned with the ratio of the intensity of the light emitted from a_1 and a'_1 respectively, the heating being the same for all the illuminated cubes on the one hand and for all the unilluminated ones on the other, the actual intensity E_0 emitted by each cube, which may possibly be diminished by a rise of temperature, does not enter into the results. Secondly, in the eye observations, the various combinations of screening were brought about with considerable rapidity, sufficient to prevent the possibility of any such effect due to changes of temperature arising. No doubt some of the light from A_2 is absorbed by A_1 in the determination of α and β for A_1; any change of temperature, however, by this means would necessarily be slow, and consequently its effect, if any, small.

Photographic Method.

The following set of experiments was first carried out.

It was afterwards found not to be altogether satisfactory on account of the necessity in these cases of superposing two photographs, and taking the resultant effect to be proportional to the sum of the separate ones. The experiments, however, are of some interest in revealing this fact: that when considerable differences in intensities have to be dealt with the resultant effect of superposing two photographs is not proportional to their sum. (It has not been considered necessary to reproduce these particular photographs here.) Captain ABNEY has previously shown that this is so.

The first photograph taken, which we shall call Photograph A, consisted of five successive images, on the one plate, corresponding respectively to a gradual alteration in the width of the slits. It was really a blank experiment to test whether the illumination was uniform or not.

All the four cubes were exposed to the exciting illuminations.

(A.)

	s'.	s.
1	7·5	8
2	8	8
3	8	7·6
4	8	7·2
5	8	6·8

The table shows the width of the slits for each of the five photographs. The nearest approach to equality was obtained in 2 and 3, and the relative intensity was reversed. The exposures were twelve minutes each. The plate was, however, considerably fogged. The next plate (B) was taken in the same way as before, but the width of the slits was diminished.

(B.)

	s'.	s.
1	5·5	5·0
2	5·25	5·0
3	5·0	5·0
4	4·75	5·0
5	4·5	5·0

The equality was here between 2 and 3. The photographs were still too dense, and the fogging too great, to make it possible to say with any degree of accuracy which way the inequality, if any, went; and it was really difficult to say if there was any difference between 3 and 4.

(C) was taken with an experiment of six minutes.

In this case the equality was between 3 and 4.

It was not possible to obtain a greater accuracy than 5 per cent. in any single plate, but it did not seem necessary in the determination of the absorption to attain even to this.

In order to test whether the absorption was the same whether the substance was fluorescing or not, the experiment was arranged in the following way:—

1. A photograph is taken with the screen, as shown in fig. 3. Let p be the ratio of intensity of the light emitted by a_1' to that emitted by a_1; then

$$\frac{E_0}{E_0(1+\alpha)} = p_1.$$

2. If p_2 is the ratio of the intensity of the light emitted by a_1' to that emitted by a_1 in the arrangement fig. 5, then

$$\frac{E_0\beta}{E_0(1+\alpha)} = p_2.$$

Hence

$$\frac{(1+\beta)}{(1+\alpha)} = p_1 + p_2,$$

and if $\alpha = \beta$,

$$p_1 + p_2 = 1.$$

The experiment is then performed by first determining p_1, and putting $p_2 = 1 - p_1$, and observing whether the two lights so obtained are of equal intensity.

Again p_2 is first obtained, and p_1 put $= 1 - p_2$, and equality again looked for.

In the first case it is found necessary to diminish s', or widen s, to obtain equality, and since the radiation from a_1 and a'_1 are inversely as the width of the slits, it follows that the real value of p_2 is greater than the calculated one, and in the second it is also found necessary to diminish s' or widen s, which shows that $p_1 + p_2 > 1$, or that $\frac{1+\beta}{1+\alpha} > 1$, and therefore $\beta > \alpha$. Hence the absorption is greater when the substance is fluorescing than when it is not, α and β being the coefficients of transmission.

To test this photographically, first of all an exposure is given when the screening of the cubes is as in (1), and then, without altering the position of the camera, the screening is arranged as in (2). The slits are such that $s' = 2s$, since we want the ratio $\frac{1+\beta}{1+\alpha}$, not $\frac{1+\beta}{2(1+\alpha)}$. Thus, if the photographic effect be proportional to the time and the intensity, the effect in the first instance on the photographic plates may be represented thus:

E_0	$E_0\frac{(1+\alpha)}{2}$

and in the second

$E_0\beta$	$E_0\frac{(1+\alpha)}{2}$

Hence the resultant effects, when superposed, are

$$E_0(1+\beta)\,; \qquad E_0(1+\alpha).$$

The camera is then slightly raised, s' is made equal to s, all the screens are removed, and a photograph is taken on the same plate with an exposure merely equal to that of each of the other two, the object being to obtain on the one plate a comparison, not merely with reference to the absorption, but also with that of the illumination. The effects on the photographic plate ought to be as follows:—

a	$E_0\ (1+\beta)$	$E_0\ (1+\alpha)$	b
c	$E_0\ (1+\alpha)$	$E_0\ (1+\alpha)$	d

If there is no change of absorption (a) ought to be of the same intensity as (b). As a matter of fact, it was always found to be much denser in the negative. The intensities of (b) and (d) were never exactly equal, but, on the contrary, (d) was always darker than (b). Now, the width of the slit for (d) was double that for (b), but the exposure was half, which shows that if we double the intensity of the light to which a photographic plate is exposed, the exposure must be less than half in order that the same effect should be produced. In other words, the photographic effect is not proportional to the intensity and to the time conjointly.

The actual width of the slits and the exposures in one particular instance were as follows :—

		s'	s	*Exposure*
Superposed	(1)	4	2	8 m.
	(2)	4	2	8 "
	(3)	4	4	8 "

The relative intensity of (a) and (c) was not constant, which shows that the average illumination may be different at different times, and it was consequently necessary to make comparisons of photographs taken simultaneously, the symmetry of the illumination having first been secured.

Fifteen plates were obtained, which are in the possession of the Royal Society and can be inspected.

Three photographs show the degree of approximation in the uniformity of the illuminations.

Some others exhibit the remarkable difference in the relative intensities under conditions such that if there were no change in the absorptive power the two intensities should be equal.

Three photographs show the superior and inferior limits of the value of α, the A_2 cube being screened, and the slits are $s = 4$, $s' = 2{\cdot}5$.

The relative intensities as given appear to be the nearest approach to the limits in the width of s' we should wish to arrive at. Thus we obtain for α the limits as follows :—

$$1 + \alpha < \frac{4}{2{\cdot}7}\,; \quad \text{therefore} \quad \alpha < 0{\cdot}48,$$

$$> \frac{4}{{\cdot}8} \qquad\qquad > 0{\cdot}43.$$

The most probable value for α obtained by the eye observations p— was 0·455.

Three other photographs give the limits for β, A'_1 and A_2 being in this case screened.

s lies between 3 and 3·5, so that

$$\beta > \frac{3}{4}, \qquad i.e. \qquad \beta > 0{\cdot}75,$$
$$< \frac{3{\cdot}5}{4} \qquad\qquad < 0{\cdot}89,$$

the value with the eye observations p— being 0·786.

Assuming the value of α to be 0·48, and that there is no difference between it and β, we obtain

$$\beta/(1+\alpha) = 0{\cdot}32.$$

Consequently if we screen A'_1 and adjust

$$s = 1{\cdot}3,$$
$$s' = 4{\cdot}0,$$

we should obtain equality of intensity on a photographic plate. This, however, does not appear to be the case, as shown in a photograph in which two successive images of the horizontal slit are given, one being the result of reversing the screws and screen, so that A_1 was for the second image sheltered from the illuminations, and A'_1 exposed, and

$$s = 4{\cdot}0,$$
$$s' = 1{\cdot}3.$$

It shows, moreover, that a reversal in the arrangement also reverses the effect.

Another plate exhibits the effect of superposing two such photographs, showing the absence of want of symmetry in the illumination.

Some other photographs show the equality of illumination and change of absorption from the calculated values, and two others the result of superposing two photographs in the following way.

Firstly, A'_1 is screened, and $s = s' = 4$; and an exposure of 30 minutes gives an effect nearly proportional to $E_0\beta$ on the left and $E_0(1+\alpha)$ on the right. Then s is closed completely, and the screen altered from A'_1 to A'_2, and an additional exposure is given without changing the position of the photographic plate, so that an increase proportional to E_0 is produced on the left. Now, since β does not differ so very much from unity, we may take the resultant effect as equal to the sum, though in reality, as shown on p. 103, it is less. The effect on the left side of the plate is then proportional to $E_0(1+\beta)$, and that on the right due to a single exposure to $E_0(1+\alpha)$, and if $\alpha = \beta$, these two should have been equal. The plates show that they are not, but give $\beta > \alpha$. This is clearly the simplest method of exhibiting the phenomenon. If the photographic effect were proportional to the intensity the difference would clearly be more marked.

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