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### XXIX. The dependence of the intensity of the fluorescence of dyes upon the wave-length of the exciting light

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XXIX. *The Dependence of the Intensity of the Fluorescence of Dyes upon the Wave-Length of the Exciting Light.* By S. I. VAVILOV, Lecturer in Physics at the University of Moscow \*.

THE connexion between the energy of exciting light and the intensity of fluorescence can be expressed on the ground of a precisely established experimental law † as

$$\int_0^{\infty} f_{\lambda_f} \cdot d\lambda_f = F = \kappa \cdot I_{\lambda} \cdot \alpha_{\lambda} \cdot \Delta\lambda, \dots \dots (1)$$

where  $f_{\lambda_f}$  is the energy of fluorescence corresponding to the interval of wave-lengths of fluorescence  $d\lambda_f$ ,  $F$  the integral energy of fluorescence,  $I_{\lambda}$  energy of exciting light,  $\alpha_{\lambda}$  the part of the light absorbed by the fluorescent dye in a finite small interval  $\Delta\lambda$ . The coefficient

$$\kappa = \frac{F}{I_{\lambda} \cdot \alpha_{\lambda} \cdot \Delta\lambda} \dots \dots \dots (2)$$

gives the energy of fluorescence per unit of absorbed energy; we shall call it "specific fluorescence." The value of  $\kappa$  is generally a complicated function of  $\lambda$ . The first stage of the problem which arises here is the dependence of  $\kappa$  upon  $\lambda$  within an isolated absorption-band. An attempt at an experimental solution of this problem was made by Nichols and Merritt ‡. These authors found that the specific fluorescence of Eosin and Resorufin increases towards long wave-lengths, for Resorufin by 2.7 times (at the change of wave-length of exciting light from 520  $\mu\mu$  to 600  $\mu\mu$ ) and by 1.63 times for Eosin (480  $\mu\mu$  to 560  $\mu\mu$ ). The authors have stated a generalization of these results § without giving a theoretical explanation.

We suppose that the question of the dependence of  $\kappa$  upon wave-length inside an isolated absorption-band is closely related to the problem of the nature of these bands in liquid and solid bodies, and has equally considerable significance for the theory of dispersion and absorption as well as for its bearing upon the theory of fluorescence.

The fundamental law (1) shows the secondary character of fluorescence, which is regulated by the value of the energy accumulated in the given molecular resonator. In

\* Communicated by the Author.

† Cf. J. Hattwich, *Wiener Ber.* Bd. 122. Abt. 11 a (November 1913).

‡ E. L. Nichols and E. Merritt, *Phys. Rev.* I. xxxi. pp. 376, 381 (1910).

§ E. Merritt, *Phys. Rev.* II. v. p. 328 (1915).

the most probable supposition that such secondary processes as fluorescence and photochemical effect are conditioned exclusively by the intrinsic energy of the resonator and its constant mechanism, the value of  $\kappa$  must be constant for the whole region of absorption: *i. e.*, for a physically simple absorption-band. Such a conclusion is maintained by the old resonance theory of fluorescence of Lommel\* and the modern theories which consider this phenomenon as a tertiary process of lighting which accompanies this or that process of dissociation of molecules †. A somewhat different result is given by the theory of Einstein, which will be mentioned later on.

From our standpoint, the inconstancy of  $\kappa$  inside an absorption-band is an indication of its physical complexity. Such a band is a result of a superposition of several bands belonging to resonators of different types: *i. e.*, with a different  $\kappa$ .

The classical theory of dispersion and absorption in all its modifications is forced to apply broadly the sign  $\Sigma$  in the explanation of absorption- and dispersion-bands of liquid and solid bodies ‡, which allows us to introduce any number of new empirical constants. The liberty in this operation is practically unlimited. It is essential that none of the experimental curves can be considered from this standpoint as a physically simple one. In all these cases we can, therefore, expect a variability of  $\kappa$ . As a criterion can be used also another secondary process accompanying the absorption of light—the photochemical effect, as was shown by Lasareff §. Therefore the experimental result of Nichols and Merritt is an argument in favour of the classical theory of dispersion and absorption.

Another supposition about the nature of broad absorption-bands was proposed by Kravec|| and qualitatively by Webster ¶. Their supposition consists in that occasional influence of fields of surrounding moving molecules (or parts of the same molecule) can in some way modify the frequency of a resonator towards both sides. The molecules will be distributed along the frequencies following the law

\* E. Lommel, *Wied. Ann.* iii. p. 251, § 19 (1873).

† E. Merritt, *loc. cit.*

‡ Cf. H. Kayser, *Handbuch der Spectroscopie*, Bd. iv. p. 457 ff. B. J. van der Plaats, *Ann. d. Phys.* xlvii. p. 429 (1915).

§ P. Lasareff, *Ann. d. Phys.* xxiv. p. 661 (1907).

|| T. R. Kravec, 'The Absorption of Light in Solutions of Dyes, Moscow, 1912, p. 106.

¶ D. L. Webster, *Phys. Rev.* II. iv. p. 177 (1914).

of probability. The experimental curve of absorption is therefore a probability curve, enclosing the family of theoretical curves with a variable parameter—its frequency. For an explanation of the experimental curves from the standpoint of this hypothesis it was unfortunately necessary to suppose at least two types of resonators. Therefore in this theory the absorption-band of dyes is also a complex one.

Many experimental facts and theoretical consequences necessitate a fundamental revision of the classical theory of dispersion and absorption. This is required by a consequent quantum theory, by a complete vagueness of the problem of the nature of damping constant, etc. Still we consider that the question of the physical simplicity or complexity of an absorption-band can be solved independently of this or other modification of the theory of absorption. The way of solution is already indicated; it is an experimental determination of coefficients characterizing the secondary processes of absorption inside the considered band.

Einstein's theory of the simplest photochemical reactions\* leads to the result that the coefficient of the velocity of reaction must be inversely proportional to the frequency of the active light. Considering in accordance with modern theories the fluorescence as a production of light accompanying the simple reaction of dissociation, we can hypothetically apply this conclusion to fluorescence. Therefore we can expect the following dependence of  $\kappa$  upon  $\lambda$  inside a simple absorption-band :

$$\kappa = a \cdot \lambda,$$

where  $a$  is a constant. For a complex band,  $\kappa$  must be a totally different function of  $\lambda$ .

Thus we can interpret the experimental results of computation of  $\kappa$  on the following lines :—

(a) If  $\kappa = \phi(\lambda), \dots \dots \dots (3)$

where  $\phi$  is a more or less complicated function of  $\lambda$ , the absorption-band is a physically complex one.

(b) If  $\kappa = a \cdot \lambda, \dots \dots \dots (4)$

the band is a simple one and the theory of Einstein is true.

(c) If  $\kappa = \text{const.}, \dots \dots \dots (5)$

the band is a simple one and the theory of Einstein is not true.

\* A. Einstein, *Journ. d. Phys.* V. iii. p. 277 (1913).

## EXPERIMENTS.

As has been already mentioned, Nichols and Merritt found that the specific fluorescence of Resorufin and Eosin increases towards long wave-lengths. The scope of the present investigation is to state how general is this result. It is of some interest to note that when this increase is a general rule we can give a simple explanation to the law of Stokes. From this standpoint, the fluorescence is excited chiefly or exclusively by the absorption in a small band situated towards long wave-lengths relatively to the resulting maximum of a complex band.

The appearance of the curve for Resorufin suggests that the band is complex, while in addition to the principal maximum, there are three secondary maxima from the side of the short waves\*. The band of absorption of Eosin investigated by Nichols and Merritt differs considerably from that of Eosin studied by us (fig. 3). Unfortunately, among six Eosins at our disposal we did not find a dye very closely resembling the Eosin of Nichols and Merritt. These authors excited fluorescence by a Nernst glower which took the place of the slit of a large spectrometer. The narrow regions in the spectrum thus formed were used in exciting the solution studied. The intensity of fluorescence so excited was evidently very feeble; this can explain the very considerable deviations of computed points, especially in the case of Eosin.

The diminution of errors of observation had a considerable significance for us when proposing to test the equation of Einstein (4), where the systematical deviations do not exceed 15-19 per cent. in the conditions of the experiment. Therefore it was necessary to increase the intensity of fluorescence and to avoid the errors in determining the wave-lengths of the exciting light which are almost inevitable in a prismatical resolving of light, especially in the yellow-red part of the spectrum. Therefore we applied, instead of monochromatic light, the light transmitted through the light-filters quantitatively measured.

Let us presume that the energy of the exciting source of light in the interval of wave-lengths  $\lambda \dots \lambda + d\lambda$  shall be  $I_\lambda$ . The measurement of intensity of fluorescence is made in that place in the vessel with the fluorescing solution where light has already passed the layer of thickness  $d$ . The coefficient of absorption of solutions studied in the given

\* E. Nichols and E. Merritt, *loc. cit.*

interval of waves is  $xc$ , where  $c$  is concentration. Following (1), the intensity of fluorescence in the named point of vessel will be

$$\kappa_{\lambda} \cdot I_{\lambda} \cdot xc \cdot e^{-xc d}.$$

Let further a light-filter be placed between the source of light and the vessel transmitting the part of light  $f(\lambda)$ . In this case the integral intensity of fluorescence will be expressed by

$$F = \int_{\lambda_1}^{\lambda_2} \kappa_{\lambda} \cdot I_{\lambda} \cdot f(\lambda) \cdot xc \cdot e^{-xc d} \cdot d\lambda, \quad . . . (6)$$

where  $\lambda_1, \lambda_2$  are the practical limits of the disappearance of the function

$$I_{\lambda} \cdot f(\lambda) \cdot xc \cdot e^{-xc d}$$

(these limits depend evidently upon the applied light-filter) and  $\kappa_{\lambda}$  is the specific fluorescence (2).

In the experiments of Nichols and Merritt and in the theory of Einstein,  $\kappa_{\lambda}$  is an increasing function of  $\lambda$ . In both cases we can apply to (6) the theorem of the middle value of a definite integral—*i. e.*, we have

$$\kappa' = \frac{F}{\int_{\lambda_1}^{\lambda_2} I_{\lambda} \cdot f(\lambda) \cdot xc \cdot e^{-xc d} \cdot d\lambda}, \quad . . . . (7)$$

where  $\kappa'$  is the middle value of  $\kappa_{\lambda}$  corresponding to  $\lambda'$ , lying between  $\lambda_1$  and  $\lambda_2$ . When  $\kappa_{\lambda}$  is a linear function (as follows from the theory of Einstein and also from Nichols and Merritt's experimental results for Eosin and also in a long interval for Resorufin), and when the subintegral function in (7) is symmetrical relatively to

$$\lambda = \frac{\lambda_2 - \lambda_1}{2},$$

then it is easy to prove that  $\kappa'$  corresponds to  $\lambda$ , through which passes the ordinate halving the area

$$\Phi = \int_{\lambda_1}^{\lambda_2} I_{\lambda} \cdot f(\lambda) \cdot xc \cdot e^{-xc d} \cdot d\lambda. \quad . . . (8)$$

In cases when the subintegral function is only approximately symmetrical (with which we are chiefly concerned),  $\kappa'$  corresponds only approximately to the halving ordinate of area  $\Phi$ . The formula (7) can be applied evidently also in

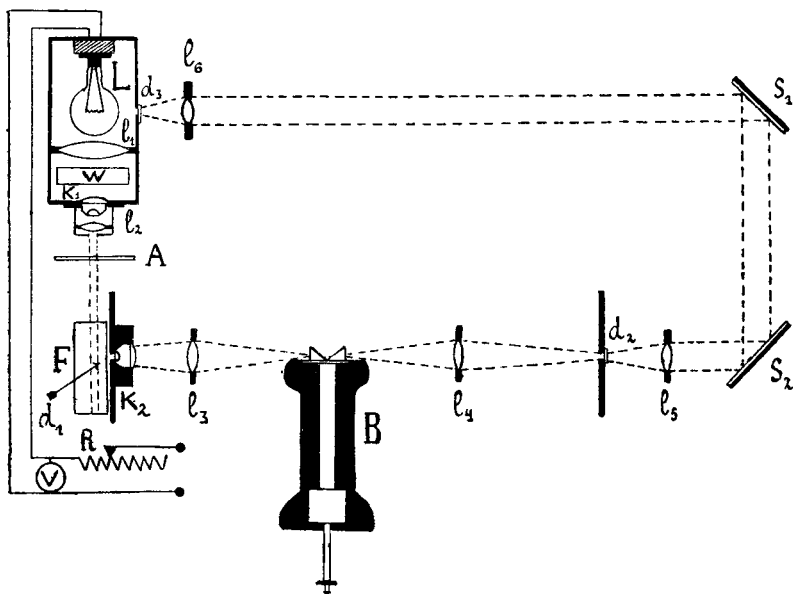
the case where  $\kappa_\lambda$  has a maximum inside of the band of absorption if the limits  $\lambda_2 - \lambda_1$  are sufficiently narrow.

The values of  $I_\lambda$ ,  $f(\lambda)$ ,  $xc$ ,  $d$  were measured,  $e^{-xod}$  was calculated. The area  $\Phi$  was determined by graphical integration by means of an Ammsler's planimeter. The error of each separate measurement necessary for the calculation of  $\phi$  is the usual spectro-photometrical one.

The method of light-filters simplifying observations unfortunately complicates calculations exceedingly.

The installation of apparatus is given in fig. 1. The image

Fig. 1.



of one of the wires of Philips's lamp ( $\frac{1}{2}$  W., 200 candles, 106 volt) is projected by a large condenser  $l_1$  through a vessel W with water upon the aperture of the Zeiss aplanatic condenser  $K_1$ . Through the lens  $l_2$  passes a practically parallel bundle of light of a considerable intensity, and through the light-filter A enters a plane-parallel vessel F containing the fluorescing solution. Through the aperture  $d_1$  in the screen the light of fluorescence is projected by means of another aplanatic condenser  $K_2$ , the lens  $l_3$ , and the auxiliary prism upon the slit of a spectro-photometer of König and Martens, B. The passage of rays from the same lamp L entering in the second slit of B is seen in fig. 1.



The voltage can be regulated by means of a rheostat R. A trial has shown that the change of voltage from 100 to 110 does not influence perceptibly the relation of intensities measured by the spectro-photometer. The vessel F by means of slides not represented in the figure can be moved with a micrometrical screw along the screen. In such a way  $d$  can be regulated. The same installation served for measurement of the absorption spectra of the dyes studied, light-filters, and for determining the distribution of energy of the exciting light. For the measurement of absorption of light-filters, the widths of the slits of the spectro-photometer were taken as 0.1–0.2 mm. (measurements of intensity of fluorescence were made with open slits, *i. e.* the spectro-photometer served rather as a photometer). Instead of vessel F a prism of total reflexion was put and the aperture  $d_1$  was closed by a ground glass. Thus the light passing light-filter A enters the spectro-photometer. The second measurement was made without a light-filter. Hence the coefficient of absorption was determined as usual. The absorption of solutions of dyes was measured in different ways : (1) by means of a vessel with Schultz's body; (2) by an immediate installation of an absorption vessel in the passage of the parallel light-bundle between  $l_6$  and  $S_1$ ; (3) for determining the slopes of the curves of absorption the measurements were made in vessels of considerable thickness (6–8 cm.).

*The Distribution of Energy.*

A Hefner's candle was used as a standard. Its distribution of energy in the visible spectrum has been carefully measured by Ångström\*, and can be expressed quite precisely through the formula of a grey radiation :

$$I_\lambda = 0.0160 \cdot \lambda^{-5} \cdot e^{-\frac{7.85}{\lambda}}, \quad . . . . (9)$$

( $\lambda$  in microns). The formula was frequently tested. The measurements of Nichols & Merritt and Coblenz† show that the perceptible deviations begin only in the red region of the spectrum, approximately from 605  $\mu\mu$  : *i. e.*, behind the limits of interval studied by us. We can evaluate the exactness of (9) according to the difference of the integral radiation of the Hefner's candle, measured frequently, and

\* K. Ångström, *Phys. Rev.*, I. xvii. p. 302 (1903).

† *Cf.* C. L. Nichols and E. Merritt, 'Studies in Luminescence,' p. 178 (Washington, 1912).

the integral radiation calculated by means of the law of Planck :

$$I_{\lambda} = \frac{2c^2\lambda}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{\kappa\lambda T}} - 1},$$

with constants changed on the basis of formula (9). The measured value of the integral radiation is

$$2.15 \cdot 10^{-5} \frac{\text{gr. cal.}}{\text{sec. cm.}^2},$$

the calculated value

$$2.74 \cdot 10^{-5} \frac{\text{gr. cal.}}{\text{sec. cm.}^2}.$$

The deviations lie, according to the above, in the red and infra-red part of the spectrum.

For the determination of distribution of energy of our source, the prism of total reflexion was put instead of the vessel F, the aperture  $d_1$  was closed by a ground glass, and a comparison was made between the intensity of the light illuminating the ground glass with that of the light entering the right slit of the spectro-photometer. Afterwards the prism was removed, and by means of an achromatic lens the image of the flame of a Hefner's candle was projected upon the ground glass in such a way that the part of the flame 1.5 cm. above the wick was projected on the aperture  $d_1$  \*. The curve of relations of measured intensities of source and candle, multiplied by (9), gives the distribution of energy of our source of light. The curve determined in such a way satisfies sufficiently the formula of grey radiation :

$$I_{\lambda} = Q \cdot \lambda^{-s} \cdot e^{-\frac{2.67}{\lambda}} \dots \dots \dots (10)$$

In Table I. are given the values of  $I_{\lambda}$  measured with those calculated by (10), wherein Q is taken as  $4.710 \cdot 10^3$ .

TABLE I.

$\lambda$	$T_{\lambda}$ meas.	$T_{\lambda}$ calc.
0.410	0.125	0.133
0.435	0.258	0.235
0.455	0.380	0.345
0.473	0.480	0.489
0.490	0.660	0.645
0.515	0.880	0.905
0.548	1.325	1.350
0.565	1.588	1.560
0.580	1.870	1.910
0.590	2.080	2.050

\* A. Becker, *Ann. d. Phys.* xxviii. p. 1029 (1909).

Measurements were repeated several times during our work, giving always the same result.

We used light-filters, partly coloured glasses, partly coloured films put between two glass plates. Some light-filters were prepared by us in collodion and gelatine films on glass. The curves of absorption of light-filters were measured at least twice.

*Dyes.*

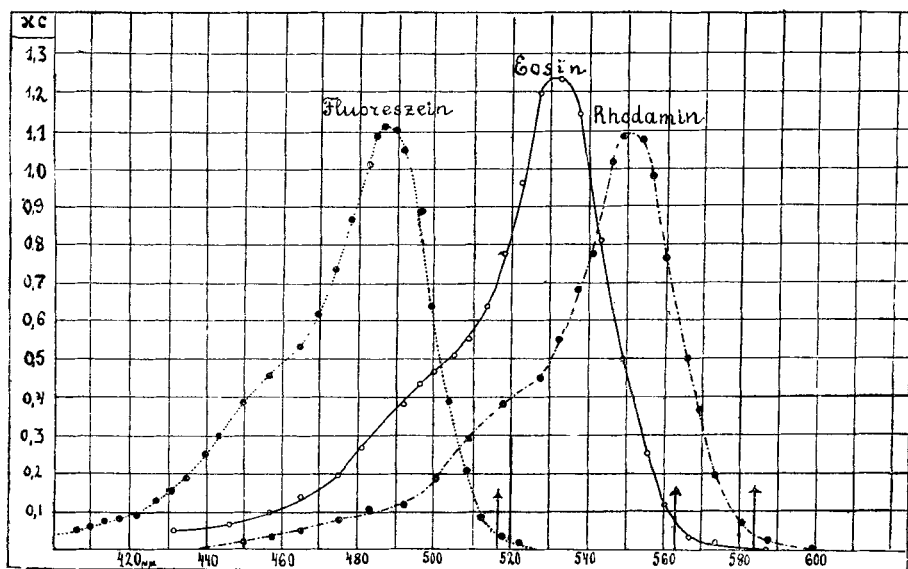
The fluorescing dyes were selected so that their bands of absorption covered the whole region accessible to visual investigation from 400  $\mu\mu$  to 600  $\mu\mu$ . Most careful measurements were made with water solutions of the following dyes :—

Fluorescein (Ferrein) + KOH  $9.7 \cdot 10^{-6} \frac{\text{gr.}}{\text{cm.}^3}$  and  $4.85 \cdot 10^{-7} \frac{\text{gr.}}{\text{cm.}^3}$ .

Eosin S extra C. (Bayer) ...  $1.2 \cdot 10^{-5} \frac{\text{gr.}}{\text{cm.}^3}$ .

Rhodamin B extra (Bayer) ...  $1.4 \cdot 10^{-6} \frac{\text{gr.}}{\text{cm.}^3}$ .

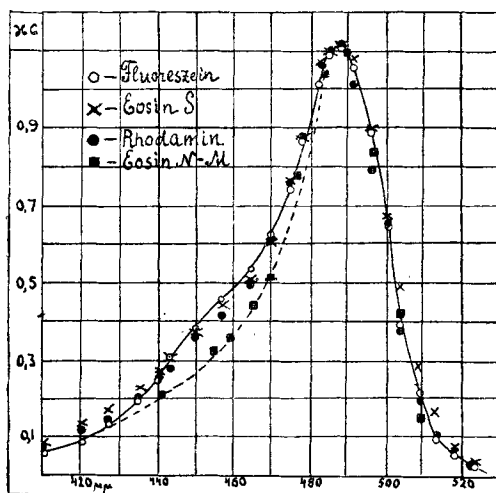
Fig. 2.



Eosin S gives a rather weak fluorescence ; still it was the only one whose band of absorption followed sufficiently that of the Eosin studied by Nichols and Merritt. In fig. 2 are

given the curves of absorption of all three dyes. The ordinates of Fluorescein correspond in the figure to  $0.163 xc$  and for two other dyes  $xc$ . The curves are perfectly monotypical, differing only in the different situation of maximum and the absolute value of  $xc$ . This can be proved by a superposition of all three curves. In fig. 3 the curve of

Fig. 3.



Eosin is removed to a distance of  $45 \mu\mu$ : *i. e.*, the interval separating the maximum of Fluorescein and Eosin. The curve of Rhodamin is removed to a distance of  $65 \mu\mu$ . The ordinates of maxima of all curves are reduced to the same value. On the same figure are marked the points corresponding to Eosin of Nichols and Merritt, maximum removed to a distance of  $38 \mu\mu$ . The established regularity allows of several conclusions being drawn:—

1. All dyes studied by us have the same mechanism of absorption in the visible part of absorption.

2. The coefficient of absorption is sufficiently approximated by

$$xc = f(\lambda - \lambda_0),$$

which is in contradiction with the classical theory for the simple band and likewise for a complex one.

3. The invariability of the form of the curves by removing their maxima to a distance of  $65 \mu\mu$ , serves as a criterion of the optical cleanness of our preparations.

4. The same fact serves, of course, as an indirect indication of physical simplicity of the bands of absorption studied.

The intensity of fluorescence for every dye is measured with 8 to 10 light-filters with a constant thickness of absorbing layer  $d$ . For Fluorescein and Eosin two measurements were made with different  $d$ . Every measurement was repeated at least three times on different days.

For ascertaining the amount of diffused light in the measured light of fluorescence, the solution of dye in the vessel F was replaced by pure water. In all cases the quantity of the diffused light was not more than 1 per cent. : *i. e.*, could be disregarded.

*Results.*

We abstain from the reproduction of lengthy tables with elements necessary for graphical calculations of  $\Phi$  on the basis of (8). The values of  $I_\lambda$ ,  $xc$ ,  $e^{-xc}$ ,  $f(\lambda)$  were taken from experimental curves for every  $5 \mu\mu$ . As an example of the subintegral function so obtained we include fig. 4, representing nine curves obtained for Eosin with different light-filters. Beside every curve is given the value of  $\Phi$ , obtained by a graphical integration in the relative units, the observed value of intensity of fluorescence, also in relative units, and the relation

$$\kappa = \frac{\phi}{F}.$$

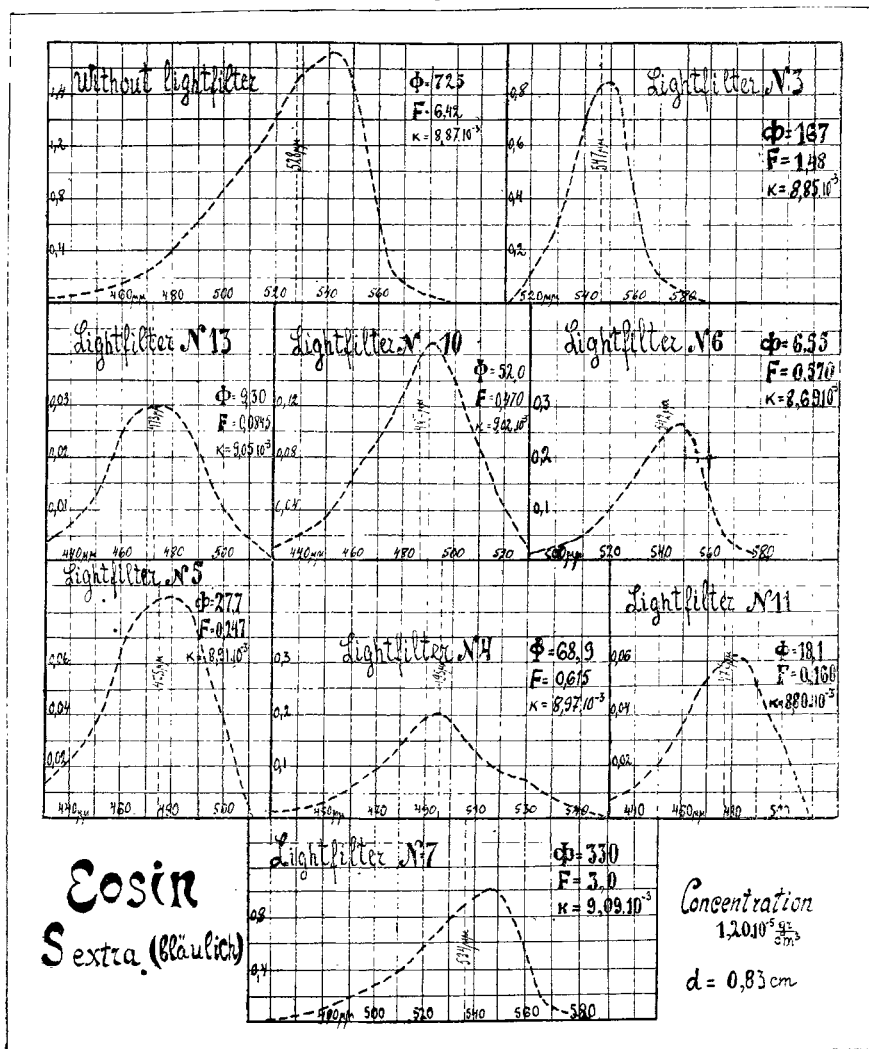
As shown in the figure, the curves are approximately symmetrical. According to the above mentioned, we can consider that  $\kappa$  so computed corresponds more or less to the wave-length through which passes the halving ordinate of area  $\Phi$ . On every curve this ordinate is marked by a dotted line. The Tables II., III., IV. contain the following data :— (1) light-filter used, (2) the value of  $\lambda$  through which passes the halving ordinate, (3)  $F$ , (4)  $\phi$ , (5)  $\kappa$ . The tables give also  $d$  and concentration. The tables correspond to the most careful measurements.

TABLE II.

Fluorescein.		$c = 3.7 \cdot 10^{-6} \frac{\text{gr.}}{\text{cm.}^3}$ ; $d = 0.80$ .		
	$\lambda$ .	F.	$\phi$ .	$\kappa$ .
5 .....	446 $\mu\mu$	2.940	61.0	4.81 $\cdot 10^{-2}$
14 .....	448	0.0579	1.23	4.70
13 ... ..	449	0.920	19.3	4.77
10 .....	453	3.70	7.50	4.93
0 .....	482	14.60	296	4.88
7 .....	506	3.62	7.45	4.86
8 ... ..	510	4.90	97.0	5.05
3 ... ..	519	0.218	4.55	4.80

From Table II. it is seen that  $\kappa$  is constant in the limits of errors of measurement of  $\phi$  and F. The greatest deviation reaches 7 per cent. There is no perceptible increase or

Fig. 4.



decrease of  $\kappa$ . According to Einstein's equation (4), it must be a linear increase to 16 per cent. within the interval 446 to 519  $\mu\mu$ .

TABLE III.

Eosin S extra.  $c = 1.20 \cdot 10^{-5} \frac{\text{gr.}}{\text{cm.}^3}$ ;  $d = 0.83$ .

	$\lambda$ .	F.	$\phi$ .	$\kappa$ .
13	473 $\mu\mu$	0.0845	9.30	$9.05 \cdot 10^{-3}$
5	475	0.247	27.7	8.91
11	477	0.160	18.1	8.80
10	487	0.470	52.0	9.02
4	495	0.615	68.9	8.97
0	528	6.42	725	8.87
7	534	3.00	330	9.09
6	542	0.570	6.55	8.69
3	547	1.48	167	8.85

TABLE IV.

Rhodamin B extra.  $c = 2.4 \cdot 10^{-6} \frac{\text{gr.}}{\text{cm.}^3}$ ;  $d = 0.83$ .

	$\lambda$ .	F.	$\phi$ .	$\kappa$ .
5	478 $\mu\mu$	0.364	10.6	$3.43 \cdot 10^{-2}$
10	492	8.25	23.9	3.46
4	513	1.67	48.5	3.45
9	544	11.4	318	3.58
0	547	29.1	809	3.60
7	552	15.8	447	3.53
3	559	12.6	339	3.70
2	579	1.05	29.2	3.60

Table III. gives the same result for Eosin. The deviation of  $\kappa$  reaches 5 per cent.; according to Einstein, there must exist the increase of 16 per cent.

For Rhodamin there is a small increase of  $\kappa$  with wave-length, which lies still inside the limit of errors of experiment. The greatest deviation is 8 per cent. This systematic deviation can be possibly explained by the existence of some discordance between the Ångström equation (9) and the true distribution of energy in the spectrum of the Hefner's candle. According to Einstein, the value of  $\kappa$  must increase in this case by 21 per cent.

In other less careful measurements of  $\kappa$  the deviations amounted to 10 to 14 per cent.

### Conclusions.

(1) Within the limits of errors of observation the specific fluorescence of our dyes is independent of  $\lambda$  within their band of absorption.

(2) According to all above-mentioned, this result is equivalent to the conclusion that the curves of absorption of our dyes are physically simple ones.

(3) The theory of Einstein is not confirmed, but the deviations required by this theory are so small that they exceed only a little the experimental errors, and we are unable to make a definite statement.

(4) The intensity of fluorescence radiated by a definite molecular resonator depends only upon the value of the absorbed energy and upon the mechanism of the resonator. In the case of an excitation by a white light we can therefore write

$$F = \kappa \int_{\lambda_1}^{\lambda_2} I_{\lambda} . x c . e^{-x c d} . d\lambda . . . . . (11)$$

(5) The result of Nichols and Merritt shows probably only the physical complexity of bands of dyes studied by these authors.

This work was carried out in the Physics Department of the Scientific Institution of Moscow, to the Director of which, Prof. Dr. P. P. Lasareff, I am much indebted for much valuable help and for his interest during the course of the work.

XXX. *Notes on Hertz's Theory of the Contact of Elastic Bodies.* By W. B. MORTON, M.A., and L. J. CLOSE, M.A., Queen's University, Belfast\*.

#### 1. Introduction.

THE elastic problem of the deformations and stresses which arise when two bodies, having continuous curvature, are pressed together was solved by Hertz† in a classical memoir. He showed that the area of contact is, in general, an ellipse, and that the displacement in the neighbourhood of the contact could be expressed by means of potential functions belonging to a certain distribution of surface-density on this ellipse: viz., that reached as the limit of a uniform solid ellipsoid. In view of the complicated nature of the mathematics, Hertz contented himself with establishing some general conclusions and with drawing a diagram of the lines of principal stress which was partly conjectural and which was afterwards found to be erroneous

\* Communicated by the Authors.

† Hertz, *Miscellaneous Papers* (Engl. trans.) p. 146. See Love, 'Elasticity' (3rd ed.), p. 191.