

ON THE THERMODYNAMICS OF FLUORESCENCE.

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THE relationship between thermodynamics and fluorescence does not seem to have been investigated hitherto in as thorough a manner as the subject deserves. In the present paper the conclusions that can be obtained without adopting special hypotheses are first carried a little further than is done by Pringsheim¹ in his discussion of the subject, and a plausible hypothesis concerning the properties of the fluorescent process is then advanced and is found to lead to an interesting relationship between fluorescence and the black body spectrum which appears to be confirmed by experiment.

Throughout the paper it will be assumed that fluorescence is a reversible process, so that thermodynamic equilibrium is possible in a system containing a fluorescent substance.

I.

Let us first consider an isothermal enclosure containing an isotropic fluorescent substance. In the latter there will be set up the usual flux of radiation corresponding to the temperature of the enclosure; let J_1 denote the normal flux per unit of wave-length at wave-length λ_1 . (J_1 is therefore the flux in vacuo multiplied by the square of the refractive index.) The existence of equilibrium now requires as usual that the radiant energy emitted by the substance shall be equal to that absorbed for each wave-length separately; but in the present case the emission consists in part of fluorescence. The latter may be denoted by

$$F_1 = \int_0^{\infty} f_{12} J_2 d\lambda_2, \quad (1)$$

where f_{12} is the "coefficient of fluorescence," *i. e.*, the fluorescent emission per unit volume and per unit wave-length at λ_1 which is excited by unit normal flux of wave-length λ_2 ; F_1 is thus the fluorescent emission excited by black body radiation at the temperature of the enclosure and may be called the *full fluorescent emission* corresponding to that temperature.

Hence, denoting by E_1 the intensity of thermal emission per unit volume at λ_1 and by a_1 the coefficient of absorption,

$$E_1 + F_1 = a_1 J_1. \quad (2)$$

¹ E. Pringsheim, *P. Z. S.*, XIV., p. 129, 1913.

Instead however of concluding, with Pringsheim, that Kirchhoff's law fails for fluorescent substances, it seems preferable to generalize the law itself as follows: *In different substances at the same temperature the absorption is proportional to the sum of the thermal and the full fluorescent emissions at each wave-length.*

It is more convenient, however, to think of the absorption as consisting of two parts:

$$a_1 = \alpha_1 + \beta_1,$$

where

$$\alpha_1 = E_1/J_1 \quad (3)$$

and is the coefficient of the "thermal absorption" which equilibrates the thermal emission, while

$$\beta_1 = F_1/J_1 \quad (4)$$

and is the coefficient of the "fluorescence absorption" which equilibrates the fluorescent emission in the enclosure. The distinction seems likely on general grounds to be a real one, but it may not be; nor can we say a priori whether the fluorescence absorption should be affected by the action of the exciting light—an effect which has been looked for repeatedly but without success.

We may now deduce certain conclusions applicable to an isolated fluorescing body. Let us suppose first that the exciting light is so adjusted that its spectrum is proportional in intensity at all wave-lengths to the black-body spectrum corresponding to the temperature of the fluorescing body. Let us assume further as an experimental fact that proportionality holds between fluorescence and exciting intensity. Then if F' denotes the intensity of fluorescent emission per unit volume, and J' , the intensity of flux of the exciting light, the former will bear to full fluorescence the same ratio that the latter bears to black-body radiation, and by (4) we shall have for any wave-length λ_1

$$F_1' = \beta_1 J_1', \quad (5)$$

where all quantities are taken for the same wave-length.

Such a distribution in the exciting spectrum never occurs in practice, but we may utilize our result as follows: let us choose that wave-length λ_2 at which the flux of exciting light, J_2' , bears the greatest ratio to the black body flux, and let J_1' in (5) be taken to bear this same ratio to black body radiation at wave-length λ_1 ; then clearly the value of F_1' given by (5) sets an upper limit to the intensity of fluorescent emission obtainable. For the fluorescent emission would have this value if the exciting intensity were increased until it stood in the same ratio to black

body radiation at all other wave-lengths as it does at λ_2 . Substituting such a value of J_1' in (5) and letting F_1' denote the intensity of fluorescence actually obtained, we have

$$F_1' \leq \beta_1 \frac{J_1}{J_2} J_2', \quad (6)$$

where J_1 and J_2 refer to black body radiation at λ_1 and λ_2 resp. If Planck's law holds,

$$\frac{J_1}{J_2} = \left(\frac{\lambda_2}{\lambda_1} \right)^5 e^{-\frac{1.44}{T} \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)},$$

or, taking $T = 293^\circ$ abs. and λ_1 of the order of $5 \cdot 10^{-5}$ cm., roughly

$$\frac{J_1}{J_2} = e^{-100 \left(\frac{\lambda_2 - \lambda_1}{\lambda_2} \right)}$$

and therefore

$$F_1' \leq \beta_1 e^{-100 \frac{\lambda_2 - \lambda_1}{\lambda_2}} J_2'. \quad (7)$$

Observational material for an exact test of (7) is lacking; but certain qualitative conclusions can be drawn. If the exciting light at the wave-length λ_2 , where it differs most from black body radiation, is of shorter wave-length than the fluorescence ($\lambda_2 < \lambda_1$), the exponential will be greater than unity and usually very large, yet fluorescence is at best relatively weak: thus the fluorescence absorption β_1 may easily be exceedingly small and impossible to detect, which is in harmony with the fact that fluorescent substances commonly show no unusual absorption in the region where the fluorescence is strongest. But where Stokes's law is violated ($\lambda_2 > \lambda_1$), the exponential becomes very small, and either β_1 must increase greatly or the intensity of fluorescent emission per unit volume must become very small, and in either case the fluorescence would be difficult to observe. Stokes's law should therefore in practice be nearly true; and as a matter of fact violations of it have not been observed for a value of $(\lambda_2 - \lambda_1)/\lambda_2$ much exceeding .03, for which the exponential in (7) becomes .034. But even over this restricted range the fluorescence can hardly be of visible intensity unless β_1 is of appreciable magnitude; and it is noteworthy that in solids and liquids, at least, violations of Stokes's law seem to be observable only where the fluorescence band is known to overlap an absorption band.

Apparently no further results can be obtained with complete rigor. But it is a characteristic feature of thermodynamics that further conclusions of great interest can often be obtained by adding certain more or less plausible assumptions; in other words, it is often possible to find

a special set of assumptions which taken together are incompatible with the second law; and while thermodynamics does not tell us which assumption is the faulty one, yet we can often decide this point with good probability on other grounds. An instance of this is afforded by Stokes's law, which can be deduced theoretically only if the fluorescence absorption is ignored.

Similarly, absorption of the *exciting* light can probably not be inferred with rigor from thermodynamical considerations—the fluorescent energy might be derived from the heat energy of the substance. But the additional assumptions required in this case are so plausible and the general likelihood of the conclusion is so strong that the occurrence of such an absorption is highly probable. Its existence will accordingly be assumed in the second part of the paper.

II.

The general argument thus leaves undecided the double question, what is the source of the fluorescent energy, and what becomes of that part of the absorbed energy which corresponds to the fluorescence and is determined by the coefficient β ; further progress is possible only on the basis of special hypotheses. We shall accordingly assume, first, that thermal emission and fluorescence are thermodynamically independent so that the thermal emission and its equilibrating absorption, determined by the coefficient α , may be left out of account without affecting our conclusions touching the fluorescence; and, second, that the energy of fluorescence is under all circumstances derived entirely from the energy of the exciting light. The latter assumption seems especially plausible in view of the fact that the fluorescent process leaves (by the general hypothesis underlying the present paper) no permanent change in the substance and should therefore be accompanied by no net heat change; the immediate action of the exciting light, if it consists in a chemical transformation or in the liberation of electrons, may well be accompanied by a reversible heat change, but the latter should be exactly reversed during the occurrence of recombination with the emission of fluorescent light.

These two assumptions lead at once to the conclusion that the energy absorbed from each monochromatic component of the exciting light in consequence of the fluorescence absorption β is equal to the energy of fluorescent emission excited by that component. For when fluorescence is excited by an isolated monochromatic beam the absorption cannot be less than the emission, there being by hypothesis no other source of energy available for the latter. But then, if the absorption exceeded the

excited emission for certain wave-lengths, the absorption from full radiation would exceed full fluorescence, whereas for equilibrium (since we may ignore thermal absorption and emission) these two quantities are equal.

Expressing the conclusion just stated in symbols, we have, for any spectral intensity of flux J_1' of the exciting light,

$$\beta_1 J_1' = \int_0^{\infty} f_{21} J_1' d\lambda_2,$$

where f_{21} denotes as before the intensity of fluorescent emission at λ_2 excited in unit volume by unit flux at λ_1 , so that the right-hand member denotes the total fluorescent emission per unit volume and per unit of wave-length of the exciting light.

Hence

$$\beta_1 = \int_0^{\infty} f_{21} d\lambda_2, \quad (8)$$

which states simply that at any wave-length the coefficient of fluorescence absorption is equal to what we may conveniently call the "exciting power," viz., the total fluorescent emission per unit volume excited by unit flux of that wave-length. This gives us a definite indication of the magnitude of the fluorescence absorption which we were not able to obtain without the aid of our special hypotheses. Since in practical cases the exciting power is always very small, the same will be true of the fluorescence absorption.

We may now combine this result with (1) and (4), obtaining

$$\int_0^{\infty} f_{12} J_2 d\lambda_2 = J_1 \int_0^{\infty} f_{21} d\lambda_2, \quad (9)$$

where J_1 and J_2 refer now to black-body radiation. This may be regarded as an integral equation for the determination of the coefficient of fluorescence $f(\lambda_1, \lambda_2)$. The range of possible solutions is too broad to allow of any rigorous conclusions, but a solution whose simplicity commends it as physically probable is:

$$f_{12} J_2 = f_{21} J_1. \quad (10)$$

If we may assume that fluorescence is proportional to the intensity of excitation, so that f is independent of the latter, then this equation would assert that the spectral intensity of fluorescence at λ_1 excited by unit flux of wave-length λ_2 bears to the reverse intensity at λ_2 excited by unit flux at λ_1 the same ratio as the intensities in the black body spectrum

at λ_1 and λ_2 resp. If this conclusion is correct, the reason for the approximate validity of Stokes's law becomes very evident.

Equation (10), assuming proportionality, lends itself readily to an experimental test even in the case of a line spectrum. Let two narrow wave-length intervals be selected, $\Delta\lambda_1$ and $\Delta\lambda_2$, each including one or more lines, and let the specimen be illuminated with portions of a continuous spectrum confined in turn to each of the chosen intervals but having in both cases the same uniform spectral intensity of flux, J' . Then the total fluorescent energy in the interval $\Delta\lambda_2$ emitted per unit volume when the exciting light lies in $\Delta\lambda_1$ will be

$$F_2' = J' \int_{\Delta\lambda_1} \int_{\Delta\lambda_2} f_{21} d\lambda_1 d\lambda_2,$$

while that in $\Delta\lambda_1$ when $\Delta\lambda_2$ is excited will be

$$F_1' = J' \int_{\Delta\lambda_1} \int_{\Delta\lambda_2} f_{12} d\lambda_1 d\lambda_2.$$

Now throughout these small intervals the black body intensity J_1 and J_2 in equation (10) may be supposed constant, so that we can substitute in the second integral

$$f_{12} = \frac{J_1}{J_2} f_{21}$$

and treat the ratio J_1/J_2 as a constant. We then obtain

$$\frac{F_1'}{F_2'} = \frac{J_1}{J_2}; \quad (11)$$

that is, the *total* fluorescent emissions excited in these two intervals of wave-length under the conditions stated are proportional to the corresponding intensities in the black-body spectrum. This conclusion could easily be tested by using a mechanical photometer such as a photoelectric cell.

Further theoretical progress is, however, possible, without loss of rigor, if we assume, as has in certain cases been found to be true, that the distribution of intensity within a fluorescence band is independent of the wave-length of excitation. We may then write

$$f(\lambda_1, \lambda_2) = \zeta(\lambda_1) \varphi(\lambda_2), \quad (12)$$

where $\varphi(\lambda_2)$ is the "exciting power" or total fluorescent emission excited in unit volume by unit flux at λ_2 , while $\zeta(\lambda_1)d\lambda_1$ is the fraction of this

emission included within $d\lambda_1$ at λ_1 . (9) then takes the form

$$\zeta(\lambda_1) \int_0^\infty \varphi(\lambda_2) J(\lambda_2) d\lambda_2 = \varphi(\lambda_1) J(\lambda_1) \int_0^\infty \zeta(\lambda_2) d\lambda_2.$$

This may be written

$$\zeta(\lambda_1) = C \varphi(\lambda_1) J(\lambda_1),$$

where C is a fixed number; substitution shows that the value of C may be assigned arbitrarily, so that this is the general solution of the integral equation. But in the physical case by definition

$$\int_0^\infty \zeta(\lambda_1) d\lambda_1 = \mathbf{I},$$

whence

$$\mathbf{I} = C \int_0^\infty \varphi(\lambda_1) J(\lambda_1) d\lambda_1 = C\Phi,$$

where Φ stands for the last integral and represents the total full fluorescent emission per unit volume irrespective of wave-length.

Hence

$$\zeta_1 = \frac{\mathbf{I}}{\Phi} \varphi_1 J_1 \quad (13)$$

and

$$f_{12} = \frac{\mathbf{I}}{\Phi} \varphi_1 \varphi_2 J_1. \quad (14)$$

In words, (13) states that *the intensity at any point in a homogeneous fluorescence band is proportional to the intensity in the black body spectrum at that point multiplied by the power of light of that wave-length to excite the band.*

All of these results hold, strictly, only for excitation by radiation of the same temperature as the fluorescing substance. In seeking an extension to other temperatures there appear to be two plausible paths along which we may proceed.

If the fluorescent process consists in the ejection of electrons from the atom with subsequent recombination accompanied by the emission of light, then, by analogy with the photo-electric effect, we should expect the rate of ejection of electrons and hence also the rate of fluorescent emission to be proportional to the exciting intensity, while the form of the spectrum should be independent of it; ζ and φ will then depend only on the temperature of the substance and J is to be taken for that temperature.

If, on the other hand, the fluorescence is due to some kind of resonance

within the atom, then it seems quite possible that equations (10), (13) and (14) will hold when J is taken for the temperature of the exciting light, the temperature of the substance affecting the phenomenon only indirectly by altering the properties of the resonators. But then a change in the temperature of the exciting light will alter J , so that if (10) holds, f must change with a change of temperature; while if (13) and (14) hold, then either ζ or φ , or both, must change with a change of temperature, since the change in J does not consist in multiplication by a constant factor. Now a change in the *intensity* of the exciting light may or may not change its temperature: if the intensity is varied by moving the source parallel to the beam the temperature remains unaltered; while if the intensity is altered by interposing a diffusing screen the temperature will be lowered. Accordingly, in the former case we should expect the coefficient f to remain constant, *i. e.*, proportionality should hold for all wave-lengths of excitation and emission; while in the latter case f would, in general, be altered and proportionality between excitation and emission could not hold for all wave-lengths, the change occurring either in ζ or in φ , or in both, in the simple case characterized by (12).

It is interesting to note that if J obeyed the Rayleigh-Lorentz law its *form* would *not* change with a change of temperature and this breakdown of proportionality would not be required by our equations. If the latter really occurs, therefore, it will probably find its ultimate explanation in the factors which lead to the failure of equipartition, whatever these may turn out to be.

Let us in conclusion turn to the comparison of the last results obtained with observation. The fluorescence of gases exhibits peculiarities strongly suggestive of resonance, but unfortunately no quantitative data seem here to be available. On the other hand, in liquids and solids the close connection usually found between fluorescence and phosphorescence suggests the first alternative described above, *viz.*, the production of some intermediate change such as ionization or a chemical change, so that the fluorescence ought to be related to the temperature of the substance rather than to that of the exciting light.

Two substances which possess an isolated unitary band and which should therefore, if the theory developed here is correct, obey equation (13), are eosin and resorufin, and fortunately the necessary data are available in a paper by Nichols and Merritt¹ in the *PHYSICAL REVIEW*. In their Table I. they give what they call the "specific exciting power" for eosin, meaning the excitation per unit of absorbed energy; hence this

¹ E. L. Nichols and E. Merritt, *PHYS. REV.*, XXXI., p. 381, 1910.

quantity multiplied by the coefficient of absorption, given in the same table, gives values of φ , which is here called the exciting power and represents the excitation per unit of light flux. For resorufin, numbers proportional to φ are obtained by multiplying the ordinates of the crosses and circles in their Fig. (93) by the corresponding ordinates of the absorption curve A in the same figure.

The experimental values of φ thus obtained are shown by the circles on the annexed plots (Figs. 1 and 2). The distribution in the fluorescence spectrum,¹ which is known to be independent of the exciting light, is shown by the curves marked ζ . We may suppose the temperature of the specimens to have been about 20° C.; the black body curve for this temperature is shown by the curves marked J (the slight variation of the refractive index with wave-length is left out of account.) Finally, the theoretical values of φ given by equation (13) in the form

$$\varphi = k \frac{\zeta}{J}$$

are shown by the curves marked ϕ , the single constant k being adjusted for a good fit. [By (8) above, $\varphi = \beta$, so that the latter curve represents also the coefficient of fluorescence absorption.]

The agreement between observed and calculated values of φ is about as good as could be expected under the circumstances. The slope of the theoretical curve over its central portion is almost exactly right and it shows indications of a maximum in the right place; it fails chiefly

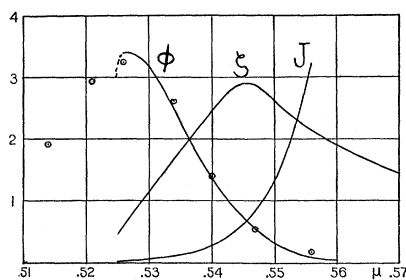


Fig. 1.
Eosin.

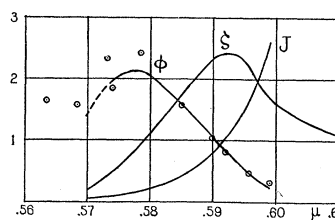


Fig. 2.
Resorufin.

at the ends, where either the fluorescence or the exciting power is small and therefore not known with certainty. A change of 10 per cent. in the slope would result from a change of 30° in the temperature or of 0.03 μ in the wave-length employed in calculating J . The final test of the theory must wait however until the region in which both quantities are experimentally known shall have been considerably extended.

¹ E. L. Nichols and E. Merritt, *Phys. Rev.*, XXX., p. 345, 1910.

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SUMMARY.

By applying thermodynamics to fluorescent substances a relationship is deduced between the coefficient of fluorescence absorption, the intensity of fluorescence and the intensity of black body radiation.

Adding the assumptions that fluorescence and thermal radiation are thermodynamically independent and that the energy of fluorescence is derived from that of the exciting light, it is concluded that in the case of an isolated unitary band

$$\zeta = k\varphi J,$$

where ζ = relative intensity in the fluorescence spectrum, φ = exciting power, and J = intensity in the black body spectrum for the temperature of the substance, all being taken for the same wave-length; and this equation appears to be confirmed by observed data.

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