was performed at various temperatures. We found that supra-conductivity is destroyed when the magnetic field at the surface of the wire reaches a definite critical value. The critical field-strength caused by the current is slightly less than H_{k1} .

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⁴ C. J. Gorter, *Arch. Mus. Teyler*, **7**, 378; 1933.

Thermal Rotations of Fluorescent Molecules and Duration of Luminescence

IMPROVED fluorometer measurements, to be published elsewhere in detail, of the duration of luminescence τ of dye molecules yielded an unexpected result, in that τ for fluoresceine in water or ethyl alcohol solution was found to be apparently greater than that in glycerine solution. This is contrary to theoretical expectations, according to which τ should be approximately proportional to the fluorescence efficiency, and it is known that this is rather greater for glycerin than for water solutions.

It seems, however, that the effect of thermal rotations of the dye molecules can account for this effect. The rotations of the molecules excited, for example, by polarised light, tend as is well known to equalise the values of all intensity components. This accelerates the decay of the intensity component I_1 parallel to the incident light vibrations and prolongs it for the perpendicular component I_2 . As a result of this, there is an increase of the degree of depolarisation from its value ρ_0 for non-rotating molecules to $\rho > \rho_0$. On the basis of F. Perrin's theory of polarised fluorescence¹, we have been able to deduce the following formulæ for the time of decay of I_1 and I_2 :

$$I_1 = \frac{I_0}{3} \left[1 + 2\rho_0 + 2(1 - \rho_0) \exp\left(-\frac{3(\rho - \rho_0)}{\tau(1 - \rho)(1 + 2\rho_0)} t\right) \right] \cdot \exp\left(-\frac{t}{\tau}\right), \quad (1)$$

$$I_2 = \frac{I_0}{3} \left[1 + 2\rho_0 - (1 - \rho_0) \exp\left(-\frac{3(\rho - \rho_0)}{\tau(1 - \rho)(1 + 2\rho_0)} t\right) \right] \cdot \exp\left(-\frac{t}{\tau}\right), \quad (2)$$

where I_0 is the value of I_1 for $t = 0$. The full argument will appear elsewhere.

From equations (1) and (2), it appears that the rates of decay are not exponential, but that they are a sum or a difference of two exponential functions. Only for $\rho = 1$ or $\rho = \rho_0$ are they exponential and corresponding to the mean life period of the excited molecules. In all other cases, for $\rho_0 < \rho < 1$, I_1 decays faster and I_2 slower than $e^{-t/\tau}$. As mentioned above, experiments have shown that for I_1 the observed time of decay $\tau_{\text{obs.}}$ of fluoresceine in glycerine solution is smaller by about 20 per cent than that for a water solution where $\rho = 1$. For I_2 , however, the difference between the $\tau_{\text{obs.}}$ for water and glycerine solutions is within experimental errors, which were about 5 per cent.

Fig. 1 shows $\tau_{\text{obs.}}$ for I_1 and I_2 for fluoresceine as a function of ρ in different glycerine-water mixtures.

FIG. 1.

Although for I_2 the differences between $\tau_{\text{obs.}}$ for water and glycerine solutions are within the limits of experimental error and therefore cannot be at present detected experimentally, it seems that the hypothesis put forward above can give at least a qualitative explanation of the phenomena observed.

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Polymerisation of Formaldehyde

EXPERIMENTS on the autoxidation of gaseous formaldehyde (at 100° C.) in the light of the mercury arc showed the existence of a rapid induced polymerisation, which continued unabated as a dark reaction on switching off the light. No oxidation occurred during this 'dark reaction'.

The cause was traced to the formation of formic acid in the illumination period. It was then found that the addition of small amounts of formic acid vapour to pure formaldehyde gas precipitated a rapid and complete polymerisation of the latter, the rate of which was uninfluenced by light. The pressure-time curves showing the progress of the polymerisation with varying concentrations of added formic acid are compared in Fig. 1. Whereas, even at so high an initial pressure of formaldehyde as 500 mm. of mercury, the thermal polymerisation normally proceeded only at a rate of about 16 mm. per hour, when 34 mm. of formic acid was present, the pressure fell at an initial rate equivalent to 2,295 mm. per hour—some 140 times as fast.

The apparatus used for these experiments contained a stopcock and a ground joint connecting the quartz reaction vessel to the glass portion of the system (which was electrically heated). Neither of these could be directly heated, and it was observed that the solid polymer separated mainly at the cold part. Experiments performed in a completely heated glass system, however, confirmed the observations made in the first apparatus—except that in this case there was a residual pressure, due probably to the presence of a gaseous polymer, and the solid polymer separated out on the hot wall.

The order of the reaction is approximately unimolecular over most of the range, and the rate is not appreciably affected by packing the vessel with