

## On the Influence of Brownian Motion on the Transfer of Energy in Solutions\*

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### A. INTRODUCTION

Several authors (1-4) have computed the distances over which energy can be transferred from the solvent to the solute by a dipole-dipole interaction in common scintillating solutions. These computations are generally based on a theory which has been developed by Förster (5) and later by Galanin (6). According to this theory the "distance of interaction" is determined by several factors. Most important however are two:

1. The overlap of the energy levels of the transferring solvent and accepting solute molecules, and the respective transition moments of these levels to the ground state.
2. The lifetime of the excited state of the transferring molecules.

As to the overlap, it is easily seen that the greater the range of common energy levels of acceptor and donor the greater the probability of resonance and hence the greater the probability for transfer of energy. This overlap is not easily estimated. Essentially one computes the overlap between the absorption spectrum of the solute and the fluorescence spectrum of the solvent. And since the fluorescence spectrum usually does not give the oscillator strength, one uses instead the mirror image (about the pure electronic transition) of the absorption spectrum of the solvent, relying on the more or less established mirror symmetry between the fluorescence and absorption spectrum. As to the lifetime

\*Work performed under the auspices of the U. S. Atomic Energy Commission.

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of the excited state of the transferring molecule, it is easily seen that if this lifetime is longer, then the probability for an interaction between the excited donor and unexcited acceptor is greater.

We have thus the means of comparing the theoretical interaction distance with that found experimentally from the transfer efficiency in the solutions. Actually one does not, of course, compare interaction distances. Förster provides a formula which is based on certain statistical assumptions and which connects the "interaction distance" with the concentration of the acceptor. Thus, what one actually does is to compare the theoretical concentration with the actual one for a given efficiency of energy transfer. All authors who have made such computations for the transfer from solvent to solute in liquid scintillating solutions have found that the actual concentrations are usually much lower than the theoretical expectations.

One way to remove this discrepancy is simply to reject the theory and to assume a different process of transfer. In fact the theory was developed for dye molecules which differ in certain aspects from the molecules considered here. Migration of energy through interaction of one solvent molecule with its next neighbors is such a process. There are, however, cases in which this process cannot be the main mechanism of energy transfer. It has been shown (3, 7) that dilution of the transferring solvent to a degree that hardly permits migration of energy through interaction with next neighbors does not impair the transfer efficiency. In these cases, a long-range process has to be assumed.

Now, some authors suggested quite early that the discrepancy between theory and experiment mentioned before could be removed if Brownian motion were taken into account. Förster's formula assumes that acceptor and donor molecules have fixed positions that do not change during the lifetime of the excited donor molecules. However, because of Brownian motion, donor and acceptor molecules could diffuse into the range of interaction during the lifetime of the excited state, even though at the instant the donor became excited they were too far apart to permit energy transfer. Estimates of this effect were somewhat discordant. Belikova and Galanin (2) using a formula developed by Vavilov for fluorescence quenching, showed that Brownian motion would probably account for the differences between the theoretical and experimental

values of the transfer efficiency. For solutions of terphenyl in toluene and anthracene in anisole, Cohen and Weinreb estimated that the effect of Brownian motion would be too small to account for the differences. These estimates depend strongly on certain assumptions which are not too easily verified. One rather arbitrary factor is the molecular radius for diffusion, which can be only very roughly estimated.

Thus, we long ago started to determine experimentally the influence of Brownian motion on the transfer process. In the meantime, other authors also attacked this problem. Hardwick (8) and Knau (9) found that Brownian motion has only an insignificant influence on the transfer process.

## B. EXPERIMENTAL

In order to investigate the influence of Brownian motion on the process of energy transfer from an excited solvent to an accepting solute molecule, the transfer efficiency has to be determined as a function of the rate at which these molecules diffuse towards each other. If the transfer is dependent on diffusion, a decrease in the viscosity of the system should be accompanied by an increase in transfer efficiency. One possible way to investigate this influence of changing viscosity might be to compare the transfer efficiencies of a solution in the liquid and the crystalline states by freezing the solution. This has certain difficulties. Usually these crystals are not very uniform; there are cracks which make the crystals rather opaque and reproducibility rather low. But in addition to technical difficulties basic objections might be raised against this procedure. It is possible that the transfer process in the crystal is different from that in a liquid. The probable anisotropy of the process in a crystal, as contrasted to the assumed isotropy in a liquid solution, may be another basic difference. A comparison between the transfer in a monomeric nonviscous solution with the process in a polymeric solid solution is questionable. The chemical change associated with the process of polymerization gives rise to entirely different transfer properties, at least in many cases. The fact that higher solute concentrations are required in common plastic scintillators than in related liquid scintillators in order to obtain equivalent efficiencies might, however, be interpreted as an indication that diffusion plays an important role in the phenomenon of energy migration in liquids.

In this work the viscosity of the system was changed by changing its temperature. Since only moderate changes in viscosity can be

achieved in the aromatic solvents commonly used in energy-transfer experiments, the solution was dissolved in a viscous solvent that is transparent to the exciting and fluorescent radiations. It is thereby possible to obtain much larger changes in viscosity. It has been shown previously (3, 7) that dilution of the transferring solvent in an inert solvent (without appreciable change in diffusion constant) does not change the transfer efficiency as long as the concentration of the solute is kept constant. Therefore, any decrease in transfer efficiency in changing from the undiluted or diluted nonviscous system to the diluted viscous one has to be ascribed to the decrease in diffusion constant.

Several systems were investigated; however the most extensive information was collected for solutions in paraffin oil, in which the acceptor was anthracene and the donor molecules were naphthalene, toluene, or anisole, respectively. Paraffin oil serves as a diluent, the viscosity of which can be considerably varied by changing temperatures. The transfer efficiencies were obtained according to a method employed by several authors. (3, 10, 11) This method consists essentially in comparing the intensity of the solution when the solute is excited via transfer from the solvent with the intensity which is obtained when the solute is excited directly by a wavelength that is not absorbed by the solvent. The anthracene was directly excited by irradiation with wavelength 3340 Å; for excitation via transfer from naphthalene, toluene, or anisole, the exciting wavelength was 2650 Å. The intensity of the exciting light was monitored by measuring the fluorescence of a solution of 1 g/liter aesculin in water. The temperature of the investigated solutions was changed by means of a commercially available thermostatted cell holder, which maintained stability of temperature within about 1°C. Before measurements, and sometimes during measurements, the solutions were deoxygenated by bubbling argon through them. It may be noticed that the quenching effect of oxygen in the viscous solutions is much smaller than in the pure aromatic solvents, an indication that the quenching process depends on diffusion.

In addition to the fluorescence measurements of the solutions in which energy transfer takes place, the fluorescence of the transferring molecules in the absence of acceptor molecules was measured as a function of temperature. We shall see later that these measurements seem indispensable for any understanding of the examined processes.

The viscosities of the solutions as a function of temperature were determined by Cannon-Fenske-Ostwald type viscometers. In order to

allow for long enough times of flow, different viscometers were used for different viscosity ranges. The overlap between the results for different ranges was excellent.

### C. RESULTS

If there is any influence of Brownian motion at all, it is more likely to be expected at low acceptor concentrations; so these seem the logical ones to use. This has the additional advantage that the direct excitation of the acceptor is small and no corrections for this effect have to be made. On the other hand, at very low concentrations the importance of radiative transfer of energy may become important, and this process of course cannot be expected to depend on diffusion.

#### 1. Transfer of Energy from Naphthalene to Anthracene

The transfer of energy from naphthalene to anthracene has been the subject of several investigations in the crystalline state, for which a very efficient transfer takes place already at very low anthracene concentrations. We investigated the transfer in a solution of 20 g/liter naphthalene and 0.5 g/liter anthracene in paraffin oil.

Figure 1 shows the variation of the viscosity of the solution with temperature. Figure 2 shows the fluorescent intensity of the solution as a function of temperature when it is excited by light of wavelength 2650 Å (curve 1) and 3340 Å (curve 2), respectively. In the first case anthracene is excited via transfer from naphthalene, in the second case it is excited directly. From these curves the transfer efficiency can be computed as a function of  $T/\eta$  (which is proportional to the diffusion coefficient), where  $T$  denotes the absolute temperature and  $\eta$  the viscosity. This function is presented in Fig. 3. From Fig. 3 (full line) it is seen that the efficiency of energy transfer from naphthalene to anthracene increases from a value of 0.53 to 0.70 for an increase in temperature from  $-5^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ , corresponding to a variation of the values  $T/\eta$  from 2.2 to  $84^{\circ}\text{K}/\text{centipoise}$ . This increase in transfer efficiency is attributed to the increase in Brownian motion which facilitates the closer approach between the molecules of anthracene and naphthalene. The effect of Brownian motion can be seen also from the comparison between the transfer efficiency in the solution in paraffin oil and the efficiency in a solution of the same concentrations in cyclohexane, which was found to be 0.88 at room temperature.

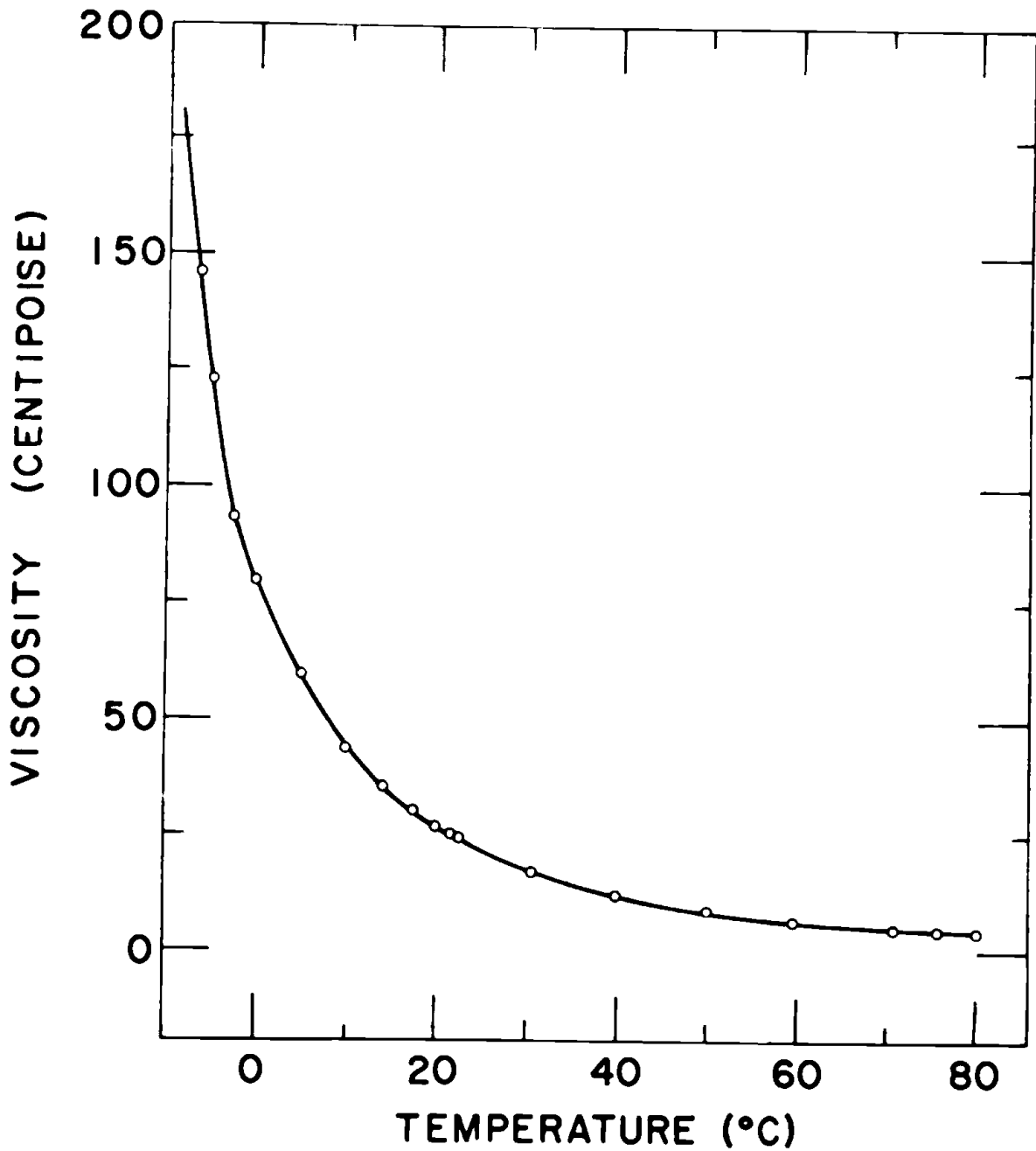


Fig. 1. Variation of viscosity with temperature of a solution of 20 g/liter naphthalene in paraffin oil.

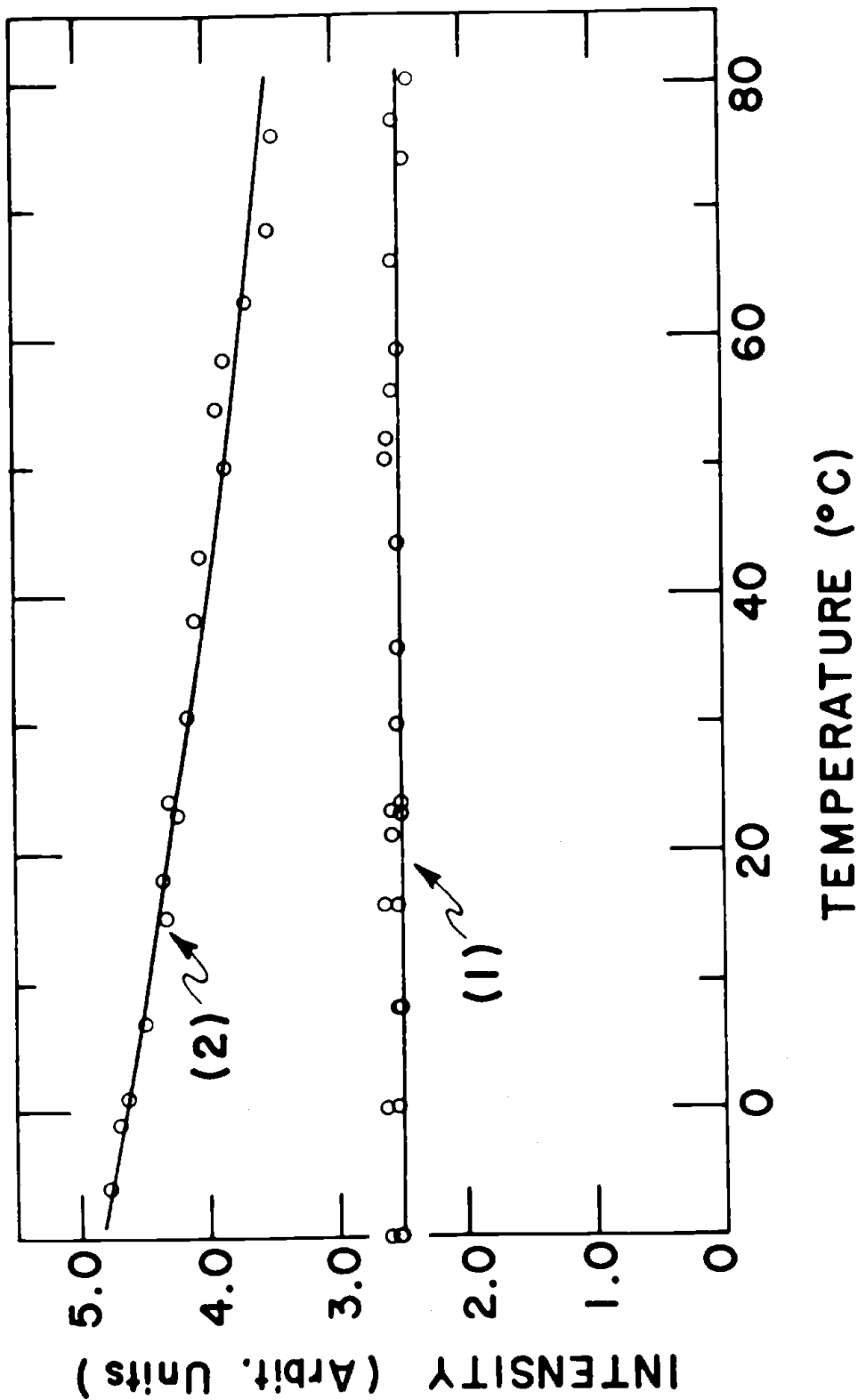


Fig. 2. Variation of fluorescent intensity with temperature of a solution of 0.5 g/liter naphthalene in paraffin oil. Curve 1: excitation with wavelength 2650 Å (excitation of naphthalene). Curve 2: excitation with wavelength 3340 Å (direct excitation of anthracene).

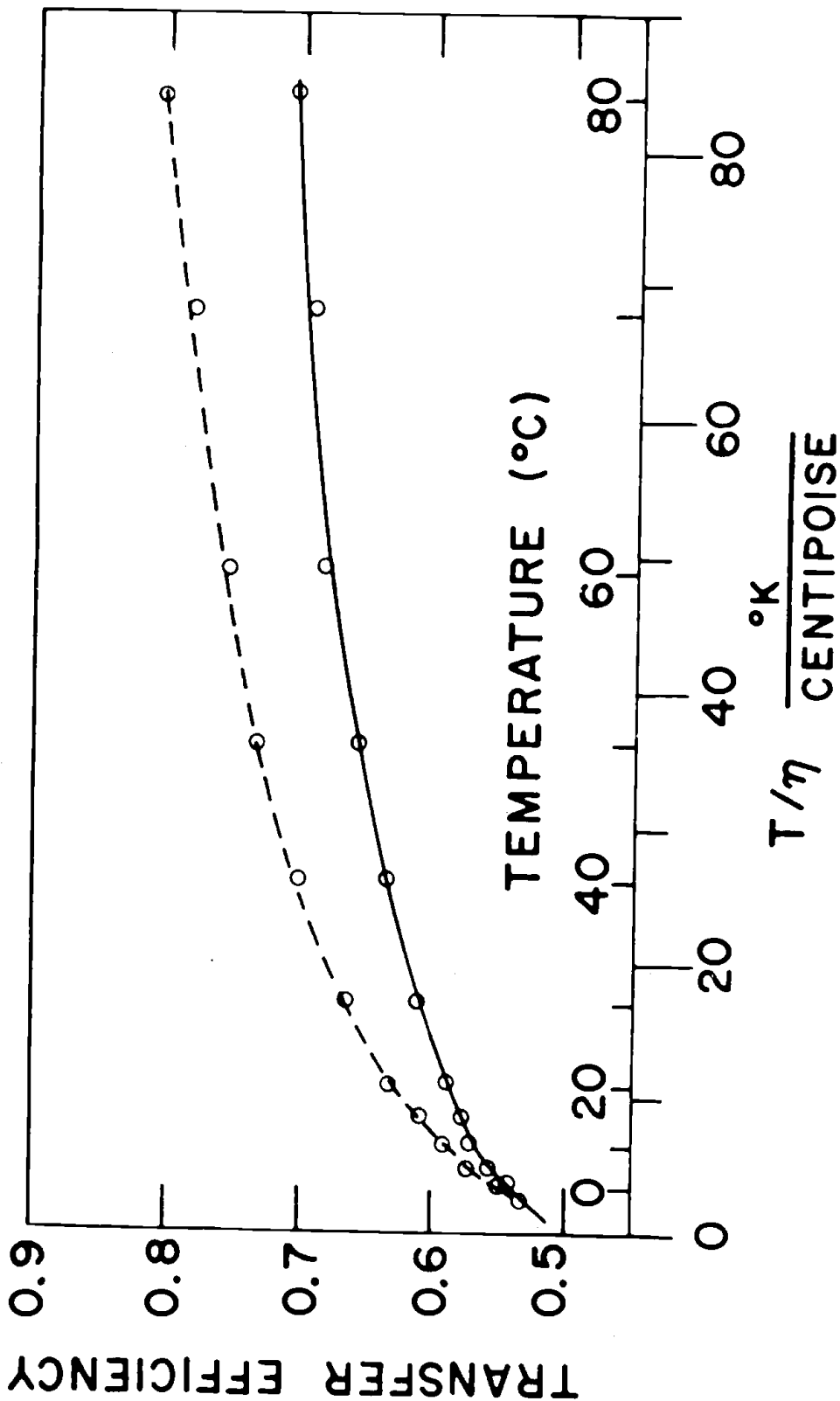


Fig. 3. Variation of efficiency of energy transfer from naphthalene to anthracene with the diffusion parameter  $T/\eta$  for a solution of 0.5 g/liter anthracene and 20 g/liter naphthalene in paraffin oil.

So far we have only observed the fluorescence of anthracene. It can be shown that practically no fluorescence of naphthalene is transmitted by anthracene under the experimental conditions. It should be stated that the fluorescent intensity of a solution of 20 g/liter naphthalene in paraffin oil is almost identical to the intensity of the same concentration in cyclohexane. From this we may conclude that self-quenching of naphthalene is low since otherwise one would expect the intensity in the much less viscous solution in cyclohexane to be considerably lower. This is an interesting feature of naphthalene. Furst and Kallmann (12) have shown that naphthalene can be used at very high concentrations as a secondary solvent in order to improve the performance of liquid scintillating solutions. This is due to the low self-quenching of naphthalene. It has also been shown by Dammers-de Klerk (13) that beyond a certain concentration an increase in concentration of naphthalene does not result in any decrease of the fluorescent yield. The question now arises as to what happens to naphthalene as a result of the change of temperature and viscosity which led to the above increase in transfer efficiency. This is seen in Fig. 4, which shows the dependence of the fluorescent intensity of 20 g/liter naphthalene in paraffin oil as a function of temperature. The figure shows a marked decrease in fluorescent intensity upon increasing temperature. We now ask to what extent the transfer efficiency is affected by the enhancement of radiationless transitions to the ground state, which manifests itself in the decrease of the fluorescent intensity of naphthalene with increasing temperature. Several authors have assumed a simple competition between energy transfer, fluorescent emission, and radiationless deactivation processes taking place in the transferring molecule. If we assume this competition between the various processes in our system, the influence of increasing temperature can be determined from the observed variation of fluorescent intensity with temperature.

Let  $I_1$  and  $I_t$  be the fluorescent intensities of naphthalene at  $-5^\circ\text{C}$  (the lowest measured temperature) and at temperature  $t$ , respectively,  $\eta_1$  and  $\eta_t$  the respective quantum yields, and  $Q_1$  and  $Q_t$  the probabilities for quenching. Let  $F$  be the probability for fluorescent emission and  $T_t$  the probability for energy transfer at temperature  $t$ . Then

$$\eta_1 = \frac{F}{F+Q_1}, \quad \eta_t = \frac{F}{F+Q_t}, \quad \frac{\eta_1}{\eta_t} = \frac{I_1}{I_t}.$$

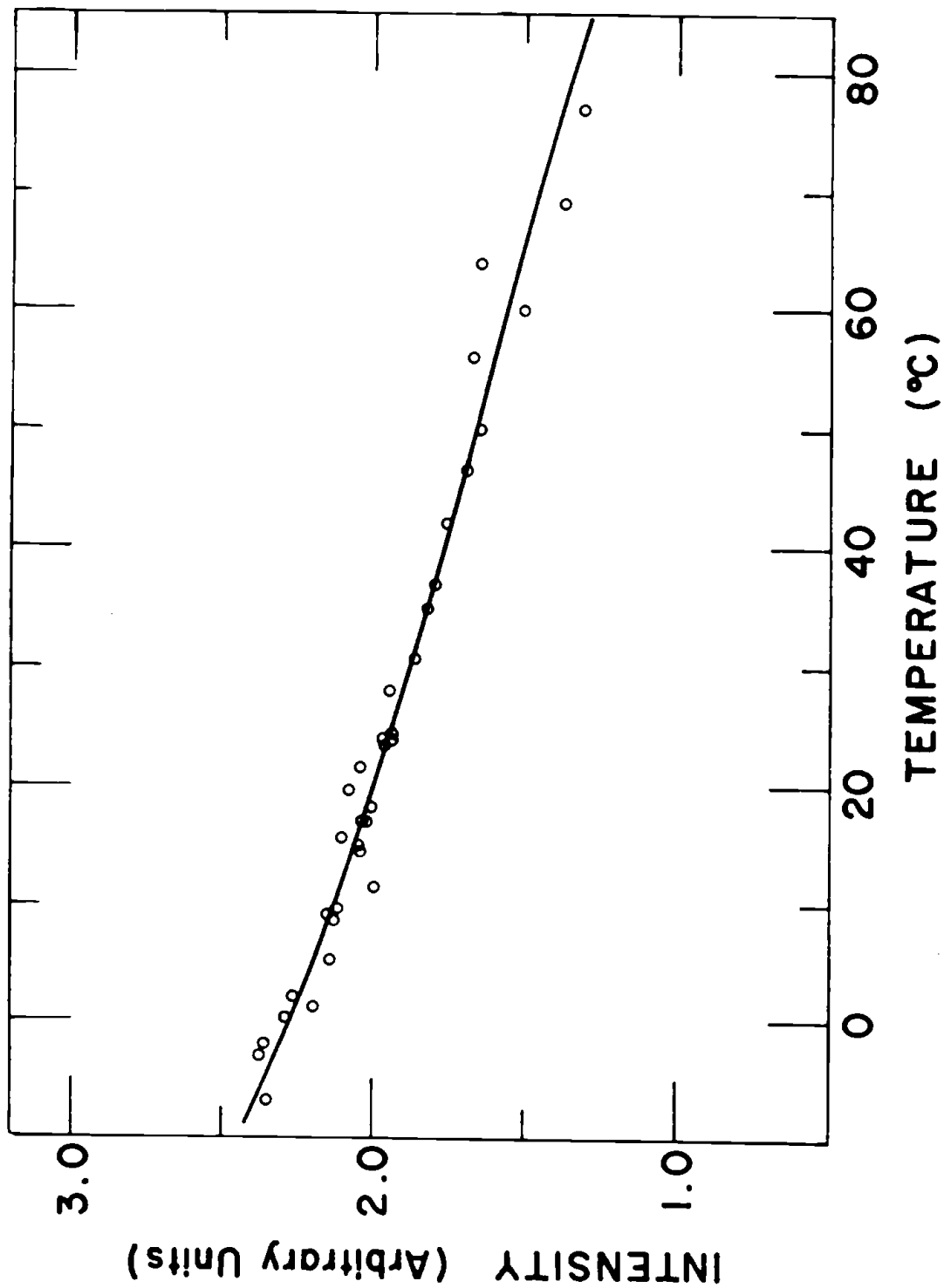


Fig. 4. Variation of fluorescent intensity with temperature of 20 g/liter naphthalene in paraffin oil.

The transfer efficiency  $\epsilon_t$  (at temperature  $t$ ) is given by

$$\epsilon_t = \frac{T_t}{T_t + Q_t + F}.$$

The corrected value  $\epsilon_t'$ , i. e., the transfer efficiency which would be observed if there were no increase in the quenching process with temperature is given by

$$\epsilon_t' = \frac{T_t}{T_t + Q_1 + F}.$$

The relation between  $\epsilon_t'$  and  $\epsilon_t$  is then given by

$$\epsilon_t' = \frac{\epsilon_t I_1}{I_t + \epsilon_t (I_1 - I_t)} \quad (1)$$

The corrected values which were thus computed are shown by the dotted line in Fig. 3.

In order to obtain the transfer efficiency in the absence of Brownian motion the results of Fig. 3 have to be extrapolated to the value  $T/\eta \rightarrow 0$ . The value thus obtained is about 0.48. The pronounced curvature of the curve at low values of  $T/\eta$  somewhat reduces the accuracy of the extrapolated value. This result shows that, although the influence of Brownian motion is rather significant, the main mechanism of the transfer process is not one of simple collision.

In order to estimate the influence of Brownian motion we have to compare the transfer probability  $T_0$  in the absence of Brownian motion with the value  $T_B$  in the presence of Brownian motion. If all the processes that compete with transfer would remain constant we would have

$$\frac{T_0}{T_0 + (F + Q)} = 0.48 \text{ in the absence of Brownian motion}$$

and

$$\frac{T_B}{T_B + (F + Q)} = 0.80 \text{ at the highest measured temperature.}$$

This would mean a change in transfer probability by a factor of 4. The transfer probability in cyclohexane is 6 times  $T_0$ .

The extrapolated value of 0.48 for the transfer efficiency in the absence of Brownian motion may now be examined in relation to the "interaction distance"  $R_0$  defined in Förster's theory. When the respective emission and absorption data of naphthalene and anthracene are introduced in Förster's equation for  $R_0$ , a value of about 40 Å is obtained. This is a much higher value than those obtained for the interaction between anthracene and the solvents usually used in liquid scintillation counters (e. g., toluene). This difference is due to the higher oscillator strength of naphthalene which manifests itself in the greater values of the absorption coefficients. It is also due to the unusually long lifetime of naphthalene (here taken to be 70  $\mu\text{sec}$ )\* which enters into Förster's equation.

From the value of  $R_0$  we can compute the concentration of anthracene that is necessary for a transfer efficiency of 0.48

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\* The decay time of naphthalene has been found by Kallmann and Brucker [H. Kallmann and G. J. Brucker, *Phys. Rev.* 108, 1122 (1957)] to be 76  $\mu\text{sec}$  for crystals and 34  $\mu\text{sec}$  for a solution of 10 g/liter in phenylcyclohexane, both under  $\beta$  excitation. After this talk was presented the decay time of naphthalene was measured (as part of a subsequent study) in this Laboratory by the technique described in references 14 and 15. The main decay part of the pulse appeared to be followed by a tail corresponding to a long decay time, which may perhaps result from the particular mode of excitation. The main decay time in deoxygenated solutions of 20 g/liter naphthalene in benzene and in cyclohexane at room temperature was found to be less than 70  $\mu\text{sec}$ . In paraffin oil, however, it was about 120  $\mu\text{sec}$ , increasing with decreasing temperature up to about 240  $\mu\text{sec}$  at  $-6^\circ\text{C}$ . The longer decay time in paraffin oil is not yet explained, although processes connected with the excitation by the solvent might, perhaps, be involved.

according to Förster's theory. The necessary concentration thus obtained is of the order of the 0.5 g/liter used in the present experiments. These results are thus not in disagreement with Förster's theory.

## 2. Transfer of Energy from Toluene to Anthracene

The system investigated was a solution of 0.5 g/liter anthracene in a mixture of 1 part toluene and 9 parts of paraffin oil. Figure 5 shows the transfer efficiency in the solution as a function of temperature and of the diffusion parameter  $T/\eta$ . The full line in Fig. 5 shows an initial increase in transfer efficiency with increasing temperature and increasing Brownian motion. For the highest temperatures, however, the transfer efficiency decreases again. This decrease can be explained, as in the case of the solution with naphthalene, by an increased temperature quenching and collision quenching of the transferring solvent, toluene. From Fig. 6 it is seen that the fluorescent intensity of toluene in paraffin oil decreases rapidly with temperature for temperatures higher than 25°C. The transfer efficiency still goes up beyond this temperature, but for the highest temperatures the quenching effect in the solvent outweighs the increase in transfer efficiency due to Brownian motion. If we again assume that the decrease in quantum yield of toluene with increasing temperature is primarily a consequence of the increasingly efficient deactivation process, the probability for emission remaining substantially constant, and if we again assume a simple competition relation between emission, quenching, and transfer of energy to anthracene, then the transfer efficiency can again be corrected according to Eq. (1). The results of this correction are shown by the broken line in Fig. 5.

Again, extrapolation of the transfer efficiency to  $T/\eta \rightarrow 0$  yields a value of about 0.28. The highest corrected value is about 0.57. The transfer efficiency in a deoxygenated solution of 0.5 g/liter anthracene in toluene has been found previously (7) to be about 0.7. Comparison of these results with those obtained with naphthalene as a transferring agent shows that in the latter system the transfer efficiency obtained by extrapolating to zero Brownian motion is higher than in the present one. As stated before, this difference can be qualitatively ascribed to the higher transition moments and longer lifetime of naphthalene as compared with toluene. The ratio between the transfer probability at the

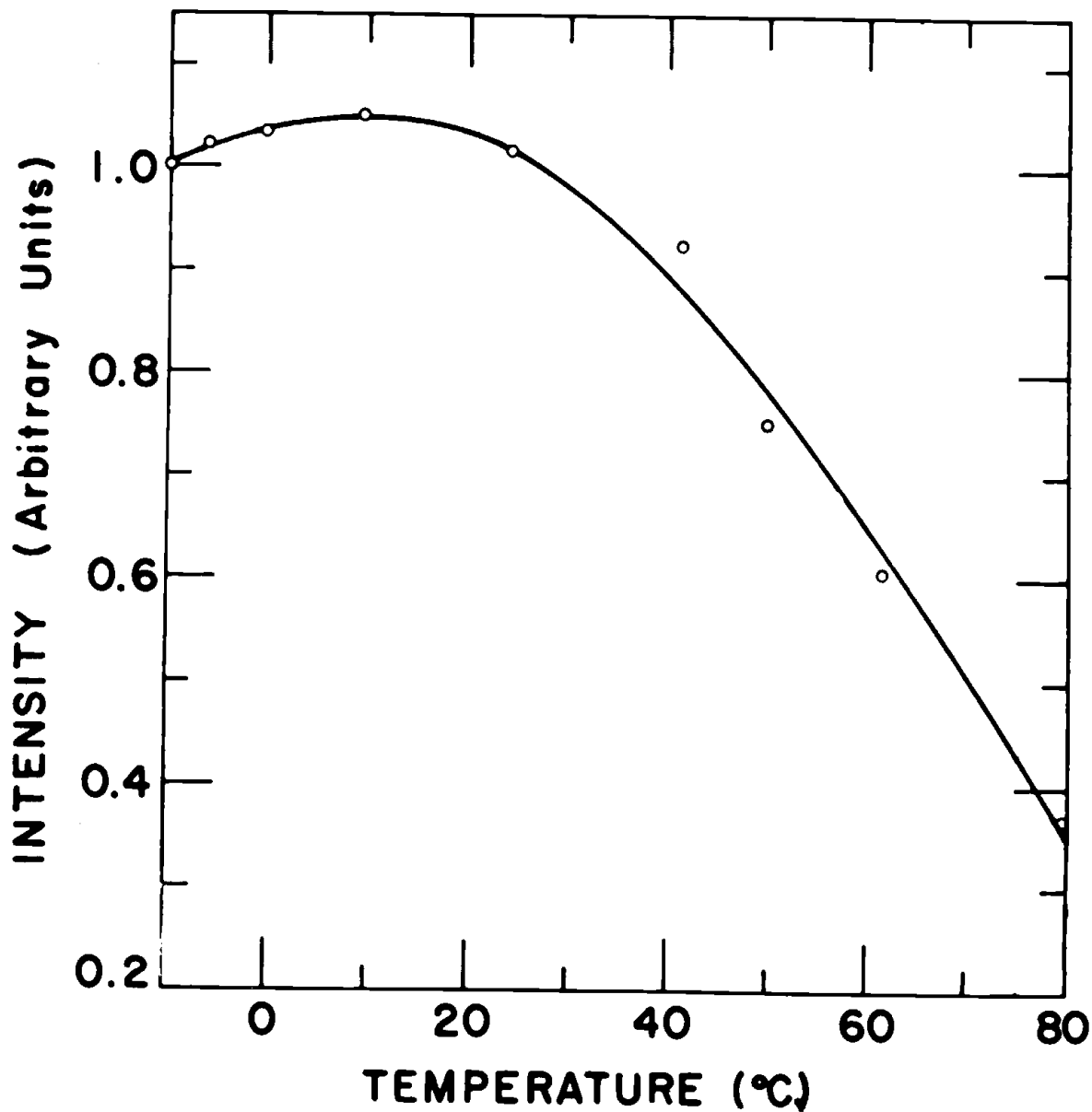


Fig. 5. Variation of efficiency of energy transfer from toluene to anthracene with the diffusion parameter  $T/\eta$  for a solution of 0.5 g/liter anthracene in a mixture of 1 part toluene and 9 parts paraffin oil.

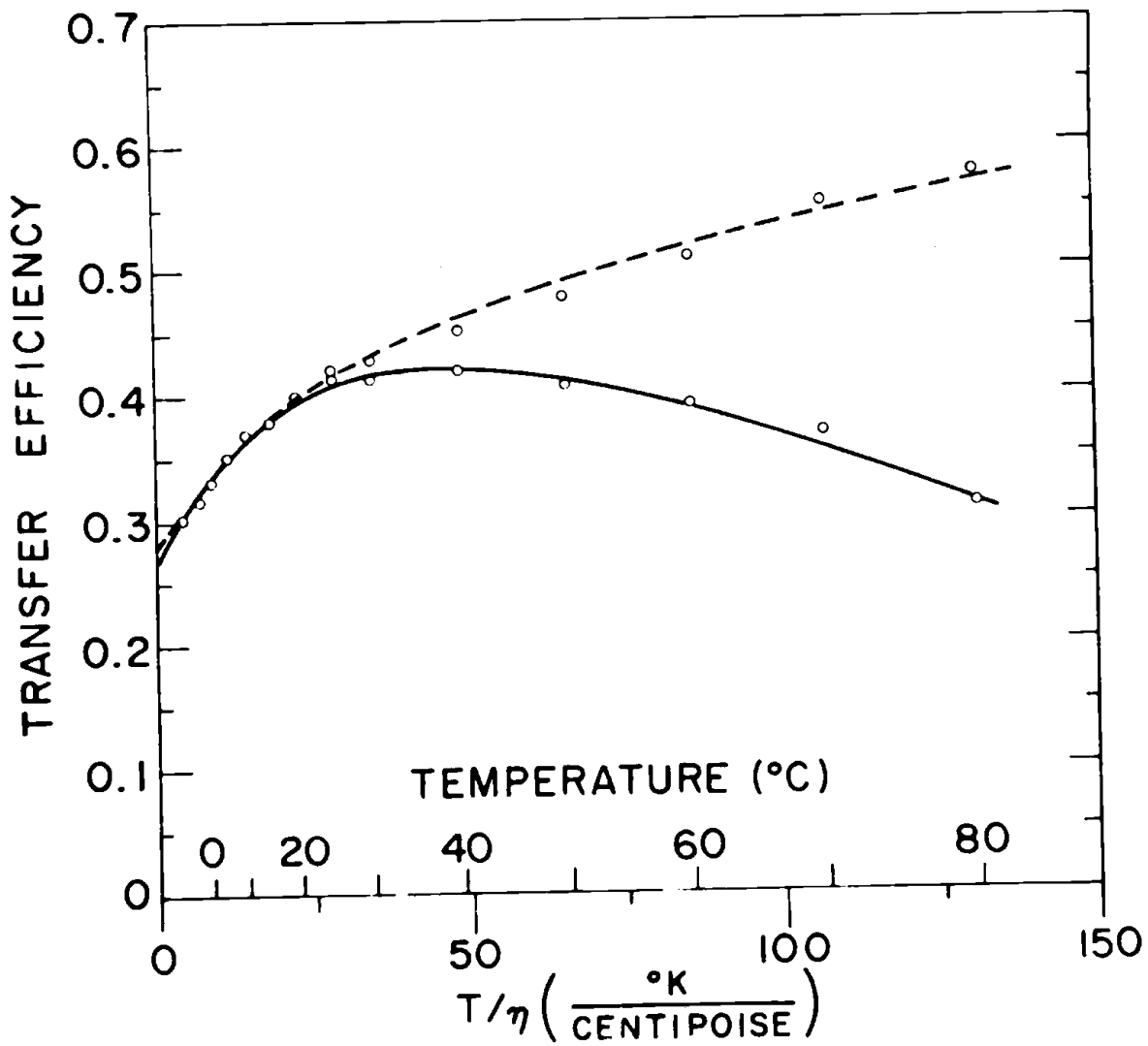


Fig. 6. Variation of fluorescent intensity with temperature of a mixture of 1 part toluene and 9 parts paraffin oil.

highest temperature and that in the absence of Brownian motion (corresponding to the extrapolated value of the transfer efficiency) is about 3 for the solution with toluene and about 4 in the solution with naphthalene. Although the parameter  $T/\eta$  at the highest measured temperature is lower in the naphthalene solution than in the toluene solution (85 against  $130^\circ\text{K}/\text{centipoise}$ ), the influence of Brownian motion in the naphthalene solution is higher, since the probability for a molecule to enter the "sphere of interaction" by diffusion increases with the "interaction distance"  $R_0$  and with the lifetime of the excited donor molecule.

In order to obtain the theoretical value for the "interaction distance" the decay time of toluene in paraffin oil was measured at various temperatures by use of an apparatus built by Swank et al. (14, 15). For these measurements the solution was excited by 75-kev electrons. Most of the exciting energy is absorbed by paraffin oil, which then transfers part of the energy to the toluene. It is assumed that the time for this transfer process is short in comparison with the decay time of toluene. The decay time of toluene at the lowest measured temperature was found to be about 32  $\mu\text{sec}$ .

The theoretical value for the "interaction distance," obtained from the absorption and fluorescence spectra of toluene and anthracene by use of Förster's theory, is about 15 Å. Accordingly, the concentration that would be necessary in order to obtain the extrapolated transfer efficiency should be about 8 times that actually employed. Thus one sees that reduction of diffusion decreases the transfer efficiency considerably, but not enough to bring about quantitative agreement with Förster's theory. The remaining discrepancy may indicate that Förster's theory does not apply quantitatively to this system, or it may have some other cause. For example, since anthracene is much more soluble in toluene than in paraffin oil, it may well be possible that anthracene molecules attach themselves to toluene and that the macroscopic viscosity which is measured does not represent the microscopic viscosity which the anthracene molecules see.

### 3. Transfer of Energy from Anisole to Anthracene

Since time is running out, I have to confine myself to a few remarks only. A very remarkable increase in transfer efficiency with temperature is observed in this system. However, the fluorescent intensity of anisole (particularly in a solution of 1 part anisole and 9 parts paraffin oil) also increases strikingly with an initial increase in

temperature. We tend to explain this by the assumption that anisole has a strong tendency to form dimers. This effect complicates the interpretation of the results considerably. The dimers may have transfer properties which are different from those of the monomers and much more experimentation is necessary in order to find the influence of dimerization on the transfer process. It may well be that similar effects occur in other systems and that they are masked by competing processes. Thus some of our familiar solutions may also hide many a surprise for the future.

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