THE BASIC PROCESSES OCCURRING IN THE LIQUID SCINTILLATOR*

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THIS talk is concerned with the basic processes occurring in liquid scintillators. First, the six subjects to be covered will be enumerated.

1. There is no doubt—and it is one of the few points which are known exactly—that under high energy excitation in some way energy goes from the solvent to the solute. In the usual liquid scintillator direct excitation of the solute by high energy radiation amounts to a negligible fraction of the total excitation. The first question to be discussed is the type of energy which is transferred from the solvent to the solute.

2. The second subject is the process of energy transfer. The mechanism is not quite determined yet because there are several possible processes which may occur and contribute.

3. Next, quenching processes in liquid scintillators will be analyzed. All who work with these scintillators know that certain impurities decrease the light output enormously even when their concentration is small. The mechanism of the quenching process will be discussed.

4. Complex solutions with several components, for instance fluorescent solutions which contain sizeable percentages of water, will comprise the fourth topic. The reasons why certain solutions containing a proper solute do not normally fluoresce under high energy excitation but do so under light, and methods of making them fluoresce will be described.

5. The fifth subject will be concerned with the period of time after excitation during which light is emitted (time constants).

6. Finally, if there is time, a little about differences in light emission produced by fast electrons and particles with a much higher density of excitation, such as alpha-particles will be discussed.

I

The answer to the first question is the following: under high energy excitation free radicals, ionized molecules, at the same time free electrons, and molecules which are excited either electronically or with atomic vibrations or with both are produced. Any of these products could possibly eventually

lead to excitation of the solute. Thus, for example, free radicals when combining to stable products could produce excited states if these are of low enough excitation energy either in the solvent or in the solute molecule when the reaction takes place close to the latter. It is known that the energy transfer process takes place within 10^{-9} sec (see part V) or possibly less, and that there is only a weak long time component in the light flashes produced under high energy excitation. It is also known that the time of recombination to a stable product is probably considerably longer than 10^{-9} sec if free radicals are separated from each other. This process is thus ruled out by the shortness of the observed emission. An immediate recombination of free radicals after their creation could lead, upon addition of energy from atomic vibrations, to an excited solvent molecule from which energy is transferred by some means to the solute. This is, however, not different from transfer of excitation energy. A direct transfer of reaction energy to the solute would essentially require a triple collision which will occur very infrequently in 10^{-9} sec. These considerations do not mean to imply that the formation of radicals is infrequent in the excitation process. It is only meant to state that apparently the contribution of their reaction energy to light emission is negligible. It may be recalled in this connection that only 5% of the total energy absorbed from high energy radiation results in light emission. A considerable portion of the total energy may be used in forming free radicals.

Ionization could contribute to light emission in the following way. A solvent molecule becomes a positive ion, and this positive charge migrates by charge exchange through the solvent from molecule to molecule in a manner similar to that to be described later for the excitation energy. When the positive charge reaches the neighborhood of a solute molecule, it may become attached to the solute molecule and remain there if the ionization energy of the solute is smaller than that of the solvent. The ionized solute molecule can thereafter recombine with a free electron and light is emitted. This process may actually occur, but its contribution to the total light emission process seems to be small. The experimental justifications for this conclusion are these: The ionization process just described should not depend specifically on the solvent since charge exchange should occur in all solvents including in particular those which are not aromatic. Most of the latter, however, are found to be ineffective for energy transfer. This is not due to differences in ionization energy since high energy induced fluorescence is found to be small in such solvents for all solutes. There are also other experiments which corroborate the conclusion about the small importance of ionization for transfer. Our investigations using light excitation when there is excitation of the solvent give results similar to those obtained under high energy excitation. In these experiments using light, ionization is excluded because of the low energy of the photons. Still another objection to ionization as an important transfer mechanism is the observed minimum speed of energy transfer. This

is too fast to be explained by a recombination process between free electrons and positively charged molecules. One may then ask why a more intense long time component of the light flash due to ionization is not found. Ionization and excitation are produced, roughly, to about the same extent when a high energy quantum is absorbed in the scintillator. Statistically, however, the recombination of a free electron with a positively charged molecule occurs in the triplet state with three times the probability of that into a singlet state. If transitions from triplet to singlet occur only rarely (which is the usual case), one then expects from ionization only a maximum contribution of 25% to the singlet state emission which is essentially the only emission observed in liquid solutions. A contribution of this order of magnitude would nevertheless still be observable. Since it is found that all long time components of high energy induced light flashes have small intensity, it is concluded that most of the recombinations of free electrons and positive charges occur rather rapidly. Probably when a free electron is produced, in most of the cases it is very quickly stopped, and it may recombine with the solvent molecule from which it was ejected before it can diffuse away. The excited atomic vibrations do not contribute directly to the transfer process since they are rapidly dissipated in the form of low energy quanta which are not energetic enough to excite the solute.

These considerations show that it is mainly electronic excitation energy of the solvent which is responsible for energy transfer. This excitation can be produced either directly, or indirectly from reactions of free radicals or recombinations of free charges. Evidence from our experiments indicates that it is mostly the state of lowest electronic excitation energy which is involved in this process; it is observed that solutes having a lowest excitation energy greater than that of the solvent are not in general excited to fluorescence by energy transfer.

<center>II</center>

The mechanism of the energy transfer process will now be discussed assuming that it is the electronic excitation which is transferred. Four possible transfer processes have been considered:

1. The excited solvent molecule transfers its energy to a solute molecule across many atomic diameters by means of a resonance process. This process is always possible if the solute has an electronic energy level below that of the solvent since the solute molecule certainly has excited energy levels (electronic plus atomic vibration) which are in close resonance with that of the solvent molecule. This process, however, cannot be of importance since the interaction energy which is responsible for such transfer is extremely small for distances of 10^{-6} cm. Such distances must be considered in order to explain by this process the observed energy transfer at 0.001M concentration. It is necessary to consider that the transition dipole for the excited electronic

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state (without atomic vibration) is extremely small as shown by absorption data. As a consequence of this smallness, the average time required for such a transition is relatively long and is certainly longer than 10^{-9} sec, which is indicated by lifetime measurements as the maximum transfer time in effective solutions.

2. The excitation energy itself migrates through the solvent.

3. The molecule which carries the excitation energy diffuses through the solvent.

Ultimately the excitation energy (in the second possibility) or the excited solvent molecule in the third possibility comes close to a solute molecule; the energy is then with great probability transferred to the solute. This final transfer can take place with a larger cross section than the geometrical cross section of the molecule but smaller than that indicated in process 1. Process 2 can be pictured as a jumping of the excitation energy from solvent molecule to solvent molecule (migration of energy). In this process the actual motion of the solvent molecules is not significant; such transfer can also occur in a solid medium. One can define a diffusion or migration constant for this process by the following equation

$$D_{\text{mig}} = \frac{l^2}{6\,\tau_{\text{mig}}} \tag{1}$$

l represents the effective diameter of the transferring molecule and τ_{mig} is the average time required for transfer from one solvent molecule to a neighboring one, which ise stimated to be of the order of 10^{-13}–10^{-12} sec. Using these magnitudes the diffusion constant for migration of excitation energy, D_{mig} is computed to be one order of magnitude greater than the normal mass diffusion constant, D_{dif}; here an actual movement of particles takes place. This latter constant characterizes process (3) where the actual molecular diffusion of the excited solvent molecule to the neighborhood of the solute molecule occurs. The comparatively large size of D_{mig} leads to the conclusion that process (2) is the more important one. The occurrence of process (2) follows directly from observations in rigid plastics where energy transfer is found to be similar to that in liquid solutions; in such plastics process (3) is excluded.

From knowledge of the constant D_{mig} the solute concentration at which half the energy reaches the solute can be calculated. According to equation (1), one thus obtains equation (2) for the molar ratio of solute to solvent $(N_{S_u}/N_{S_o})_{\frac{1}{2}}$ (which at the low concentrations usually employed is essentially equal to the mole fraction) at which half of the excitation energy is transferred.

$$\left(\frac{N_{S_u}}{N_{S_o}}\right)_{\frac{1}{2}} = \frac{1}{\pi\kappa}\,\frac{\tau_{\text{mig}}}{\tau_0} \tag{2}$$

κ represents the ratio of the transfer cross section to the solvent molecule cross section, and τ_0 is the lifetime of the excitation energy in the solvent when no transfer occurs. The concentration (molar ratio) computed in equation (2) is identical with the Q value if c in the often verified formula, $I = Pc/(Q + c)(R + c)$ which describes the increase of fluorescence, if c is expressed as a mole fraction. For process (3) it is convenient to introduce the mass diffusion constant D_{dif}; then the half value concentration $Ns_{u_{\frac{1}{2}}}$ in molecules per liter can be written as

$$\left(N_{Su}\right)_{\frac{1}{2}} = \frac{1000}{q\tau_0} \sqrt{\left(\frac{1}{D_{\text{dif}}\,v}\right)}\ . \qquad (3)$$

v is the number of diffusion displacements per second, τ_0 is the same as in equation (2), and q is the cross section of the transfer reaction. Assuming $q = \pi\, l^2\kappa$ where πl^2 is the cross section of the solvent molecule equation (3) gives a larger value for $Ns_{u_{\frac{1}{2}}}$ than does equation (2). It is difficult with present knowledge to determine how much is contributed by process (3) and how much by process (2) since the constants involved are only known to within an order of magnitude. κ is probably slightly larger than one. It may be noted here that equations (1)–(3) can with redefinition of the parameters also be applied to quenching processes and to those occurring in complex solutions (see Sections III and IV).

4. The last of the possible processes of energy transfer to be considered is that via radiation. If a solvent molecule is excited and loses its excitation energy by means of radiation, the radiation may be absorbed by a solute molecule. This would constitute energy transfer via radiation. Such transfer has been found to exist and is of importance in solutions containing more than one solute. If solute 1, Su_1, has a certain efficiency for light emission, say ξ_1 and if its radiation can be absorbed by solute 2, Su_2, which may have an emission efficiency ξ_2, then under high energy excitation, the following occurs if the concentration ratio between Su_1 and Su_2 is kept constant and Su_1 is much more abundant than Su_2. At small *total* concentration, c, energy is transferred to Su_1 from the solvent and is emitted by it with efficiency ξ_1. If the concentration of Su_2 is small enough, depending on the geometrical dimension of the vessel used for the experiment, negligible light is absorbed by Su_2 before most of the energy of the solvent is transferred to Su_1. When c is increased, the second solute begins to absorb, and since its efficiency ξ_2 is smaller than unity, the total light emission is decreased because not all the energy is re-emitted and little energy comes from the solvent to Su_2 because of its low relative concentration. Upon further increase of concentration, the light emission is found to increase again because at these concentrations energy transfer by collision between Su_1 and Su_2 sets in. In this way the effective time that excitation energy remains at molecule Su_1 is shortened, and is therefore less quenched if there is some internal quenching in Su_1 (ξ_1 is

smaller than one). Therefore a renewed increase in light emission occurs. This kind of behavior was observed (Fig. 1) for instance with a solution of *m*-terphenyl in xylene containing a small concentration of anthracene (constant mass ratio between *m*-terphenyl and 0.5% anthracene). In this case, the additional simplification in interpretation is present in that
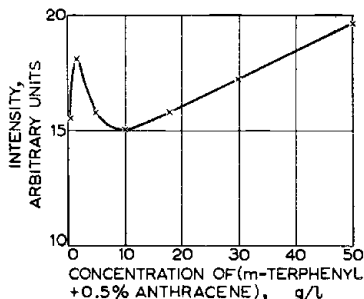

Fig. 1. Gamma-ray induced fluorescence of (*m*-terphenyl and 0.5% anthracene) in xylene.

m-terphenyl has practically no concentration (self) quenching. That of anthracene, though large, was unimportant in these solutions because of its small concentration. This experiment clearly exemplifies the competition which exists between energy transfer via radiation and via collision. Energy transfer via radiation can of course be of importance only when the emitting molecule does not have strong quenching, otherwise not enough light would be emitted in the first place.

If one applies this consideration to the system of solvent and single solute where the solvent is to be considered as the emitting molecule and asks whether energy transfer via radiation occurs, the following conclusions can be reached. Considerable transfer can occur only if the solvent has a high light emitting efficiency. Experiments, however, show that even effective solvents for energy transfer have small fluorescence. Thus, the process of radiation transfer cannot be responsible for energy transfer with high efficiency. There has been some objection to this conclusion in the literature. It has been proposed that the apparent lack of solvent fluorescence may not be due to a small ξ of the solvent but rather due to a multiple absorption and re-emission of the radiation especially if the solvent is excited in its interior portions. Then in order to explain the high yield of high energy induced fluorescence in a solution and the low fluorescent output of the pure solvent, a ξ rather close to one must be assumed, but on the other hand the low fluorescence requires absorption and re-emission processes in the solvent. The idea is that in spite of the small absorption by the solute at concentrations where energy transfer occurs, the energy is absorbed by the solute eventually because of the many re-emissions in the solvent. Experiments have been carried out with very thin layers of solution and also with solutions which were diluted by an inactive solvent.

The fluorescence of the pure solvent is still found to be weak and not enough to explain the high fluorescence obtained with a good solute. The absorption coefficient for the radiation in question is then not large enough to allow for strong absorption. By such experiments, the assumption that multiple absorptions contribute to energy transfer is excluded. In other experiments as was already mentioned, it has been shown that the lowest excited state of the solvent is mostly responsible for energy transfer. This is known since solute molecules which have an energy level above the lowest one of the solvent are not normally excited to fluorescence and since with light which excites the solvent very close to its lowest excitation energy good energy transfer to the solute is observed. In these cases almost all radiation emitted by the solvent falls outside the absorption range of the solvent and should be observed. Since only little direct radiation from the solvent is found, one must conclude that such radiation is very weak and cannot be responsible for the observed energy transfer. Energy transfer by radiation, therefore, is of only minor importance in such solutions.

To summarize our conclusions, energy transfer from solvent to solute in its major part comes about by a migration of excitation energy from solvent to solvent molecule until this energy arrives close enough to a solute molecule to which it can be transferred with a somewhat enlarged cross section compared to the geometric one. The importance of this process is indicated by the fact that in rigid systems, similar results are obtained with the essential difference that Q (the half-value concentration) is larger indicating that either energy transfer in rigid systems does not occur as quickly as in liquids (the τ_{mig} may be larger than in liquid solutions) or that the lifetime of the excited plastic molecules of the rigid medium is shorter than that of the liquid.

III

The same basic considerations which are successful in understanding the process of energy transfer are also important for the explanation of the quenching process. Two quenching phenomena are effective: one is quenching of the light emitting solute molecule and the other is quenching of the excited solvent molecule. The first quenching process is well known from studies using light excitation of the solute itself and will not be considered here. Any quenching agent which affects the solute will diminish the high energy induced fluorescence in the same way as the fluorescence directly excited by light. In addition to this solute quenching, there is also quenching of the solvent molecule which is mostly found to be greater than that of the solute. The reason for the latter can also be traced back to a migration of the excitation energy through the solvent. This energy jumps from molecule to molecule until it arrives in the neighborhood of the quenching molecule which initiates a radiationless degradation of the energy. Thus the process

leading to quenching is similar to the process leading to energy transfer; the difference is that the latter terminates with the energy being trapped by the solute molecule, whereas the former terminates with the energy quenched by the quenching molecule.

Why is it then indicated that a different mechanism is assumed to be effective for quenching of the solvent than for quenching of excitation of the solute, which latter is quenched in the course of a normal diffusion process? Certainly both types of processes occur in a solvent. Equation (2) when applied to quenching describes the half value concentration of the quenching according to the migration process and κ denotes the quenching probability (κ is the ratio of quenching cross section to solvent cross section). The diffusion process for quenching would be described by equation (3) with q now being characteristic of the quenching cross section.

From experiments which will now be described, it becomes apparent that quenching of the solvent is generally stronger than that of a solute, sometimes by a factor of more than 10. This is surprising if one uses equation (3). The lifetime τ_0 of the excitation energy (τ_0 here can refer either to the solute or solvent depending on how equation (3) is being employed) to be quenched occurs in this formula in the denominator so that the smaller the lifetime the larger is the concentration necessary to bring about quenching. Now it is known that the lifetime of the excited solvent molecules is much shorter than that of the solute; nevertheless quenching of the solvent is usually much greater than that of the solute. One could explain this by assuming that the cross section q is larger for the solvent than for the solute. On account of the short τ_0 values for solvents, however, very large q values must be assumed; this is unlikely for a quenching process which is not associated with any resonance. Another way to account for the larger solvent quenching would be to assume that quenching of the solvent does not proceed according to a process described by equation (3) but rather according to one described by equation (2) which gives a faster quenching (smaller half value concentration) than equation (3) just as in the case of energy transfer where the jumping of the excitation energy from one molecule to another one gives the faster process. To evaluate the relative importance of processes (2) and (3), one must first separate the solvent from the solute quenching.

This distinction is carried out in the following way: first one determines the quenching by a given agent when only the solute is excited by light of appropriate wavelength. In this case the observed drop is a measure of the quenching of the solute; it is only slightly dependent upon solute concentration at moderate concentrations. The decrease in emission brought about by the quenching agent is then also investigated under high energy radiation for various solute concentrations. It is generally found that even small amounts of certain quenching molecules are sufficient to shift the main rise in the fluorescence vs. concentration toward larger concentrations. When

a quencher is present in a solution greater solute concentrations are required to extract the same amount of energy from the solvent than without quencher. This follows from equation (2) in which τ_0, the lifetime of the excitation energy of the solvent, has been decreased by the presence of the quencher, and this results in an increased Q, the solute concentration required to extract half of the energy from the solvent.
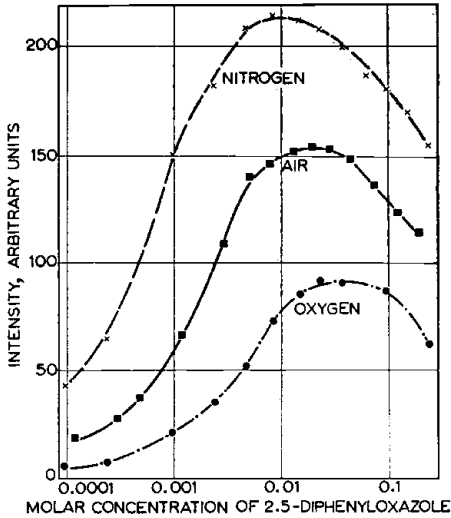

Fig. 2. Effect of nitrogen and oxygen on gamma-ray induced fluorescence of 2,5-diphenyloxazole in xylene.

Thus from observation of the fluorescence vs. concentration curves for different concentrations of quencher the quenching of the solvent can be determined. This is simplest if a solute is used which is not at all, or only slightly quenched. The curves of Fig. 2 shows the effect of oxygen on the fluorescence of a typical liquid scintillator. The particular solute is quenched by oxygen only to a small extent. There are three curves, one when no oxygen is present (carefully dried nitrogen is bubbled through the solution to remove the O_2), one when the solution is in equilibrium with air, and one when O_2 is being bubbled through the solution. It is to be noted that the presence of oxygen in the solution causes the maximum intensity to be found at larger concentrations, C_{max}. In comparing the three curves it can be seen that when there is no oxygen, the fluorescence rises at quite low concentrations, and the maximum occurs at lowest solute concentration and the maximum emission is greatest. If these curves are analyzed (fitted) according to the formula $I = Pc/(Q + c)(R + c)$ one finds that the value of Q increases when quencher concentration (oxygen in this case) is increased. According to the formula an increase in Q results in an increased C_{max} and a decreased I_{max}.

$Q = c_{\frac{1}{2}}$, the concentration where half the energy is transferred to the solute, is inversely proportional to the lifetime of the excited solvent molecule. The concentration of quencher at which Q is twice as great as when no quencher is present is that for which half of the excited solvent molecules become quenched. Removal of air changes Q considerably; indeed the oxygen content due to the solution being in equilibrium with air is found to quench more than half of the solvent molecules. Despite this strong solvent quenching, the maximum intensity (under high energy excitation), $I_{\max}$, is only slightly reduced. The reason for this is that quenching of the solvent by the quencher (oxygen) is partially compensated for by more solute being present. In this way, a relatively large amount of energy from the solvent is transferred to the solute, and therefore less energy is quenched. If there were no concentration quenching of the solute $[R \rightarrow \infty$ but $(P/R) > 0]$, quenching of the solvent would result only in a slower rise of fluorescence with concentration, but the light output at very large concentrations would not be lowered at all compared to that under better transfer conditions since by employing large enough solute concentrations the quenching of the solvent can essentially be circumvented.

The situation described for oxygen is encountered to some degree in all cases of solvent quenching. Another interesting example is the quenching of tetralin (tetrahydronaphthalene). This solvent is a very efficient solvent when it is removed from contact with air. In contact with air, peroxides are formed which are found to quench the excited solvent molecules. It is usually observed that the fluorescence efficiency of a solute molecule in this solvent is influenced only to a small extent by deterioration of the solvent. This is tested under light excitation. Under high energy excitation, however, the fluorescence decreases more the longer the solution is in contact with air, and the maximum of fluorescence is found to occur at higher solute concentrations. This behavior is similar to that which occurs for oxygen quenching. The reason for this deterioration is the increasing amount of peroxides formed while the solution is in contact with air, which quench the solvent molecules.

Quenching of solvents and solutes under various conditions is shown in Table 1. It is seen that when oxygen and carbon tetrachloride are the quenchers the solvent is much more quenched than the solute. Oxygen according to these results is a more powerful quencher than carbon tetrachloride for solutes as well as for solvents. For the quenching of xylene by oxygen it is seen that about 0.001 mole/l. oxygen is sufficient for quenching the excitation of xylene to half its value. Above it was seen that the half value solute concentration which brings about energy transfer is of the same order of magnitude. This indicates that the process of solvent quenching by oxygen and that of transfer of energy from the solvent to the solute have cross sections of the same order of magnitude. This is unexpected since energy transfer is some kind of resonance process, whereas the quenching process is not. One may conclude

that the resonance in the transfer process is not the determining factor for the cross section. The reaction rates of these solvent quenchings are thus extremely high. These findings and the preponderance of solvent quenching over solute quenching are major reasons which lead us to the conclusion that the solvent

TABLE I

Comparison of Energy Transfer and Quenching

	$\frac{1}{2}$ Value concentration $C_{\frac{1}{2}}$ mole/l.	Type of reaction
Solvent reactions	0.001 (DPO)*	Energy transfer from xylene to 2,5-diphenyloxazole in equilibrium with air
	0.0004 (DPO)	Energy transfer from xylene to 2,5-diphenyloxazole without dissolved oxygen (nitrogen bubbling through)
	0.001 (O_2)	Quenching of the solvent (xylene) by dissolved oxygen
	0.03 (CCl)$_4$	Quenching of the solvent (xylene) by carbon tetrachloride
Solute reactions	0.005–0.02 (O_2)	Quenching by oxygen of various solutes in benzene†
	0.08 (CCl$_4$)	Quenching of p-terphenyl in xylene by carbon tetrachloride

* (DPO) signifies 2,5-diphenyloxazole
†calculated from data of E. J. BOWEN, *Trans. Farad. Soc.* **50**, 97 (1954).

quenching and transfer both go according to the migration process characterized by equation (2) rather than by means of the slower molecular diffusion process (equation (3)) which is probably the only one which is important in quenching of the solute.

The consideration presented here should be considered as a first approach to the problems of quenching the solvent. More experiments, particularly some about time constants, connected with these processes are required in order to discriminate clearly between effects due to processes (2) and (3).

IV

Closely connected with the problem of quenching is the fourth subject, which will now be considered. It is very widely known that there are many

inefficient solvents which give practically no fluorescence with a solute under high energy radiation although considerable fluorescence may be displayed when the same solute in the same solvents is directly excited by light. The reason for this, we feel, is that excited molecules of these solvents have such a short lifetime that the normal solute concentrations are not great enough to extract excitation energy from the solvent, recalling that in equation (2) the concentration for half energy transfer increases as τ_0. There are many such inefficient solvents, for example paraffin oil, hexane and *cyclo*hexane. In all of them the excitation energy of the solvent molecule probably has only a very short lifetime, not long enough to enable energy transfer to come about with the normal solute concentrations employed. At considerably higher solute concentrations, however, such energy transfer has been observed to a small extent. The solubility of most solutes is too small, however, to reach the concentration range of good energy transfer.

Processes which enable the excitation energy to be eventually transformed into fluorescence in solutions which are normally not fluorescent under high energy excitation will now be discussed.

The basic idea is that one must add to these inefficient solutions a suitable substance in such concentrations that the excitation energy from the inefficient solvent can be extracted. This requires usually that it must have a high solubility in the main solvent. This substance need not be fluorescent by itself, but it must have a relatively long excitation lifetime so that this energy can be transferred to a suitable fluorescent solute under normal conditions. Substances that meet these qualifications to some extent are for instance xylene and many of the normally efficient solvents. Naphthalene which can not be used as a main solvent at room temperature because it is solid is a very effective material. The fluorescence occurring under high energy excitation when such a fluorescence enhancing substance is added to a solution in an inefficient solvent is illustrated in Fig. 3, in which the inefficient solvent is tri-*n*-amylborate and the added substances are xylene and naphthalene. The solute is 2,5-diphenyloxazole at a fixed concentration; the energy is eventually transferred to it, and ultimately it emits the light. The lifetime of excitation energy in tri-*n*-amylborate is probably so short that only very little transfer to the solute can occur; thus the intensity on the right (100% tri-*n*-amylborate) is very low. Addition of xylene or naphthalene produces a rapid increase in fluorescence. It is seen that at a molar ratio of less than 0.1 of xylene or naphthalene, the fluorescence is already close to the value obtained using xylene alone and the same fluorescent solute; this fluorescence is given by the highest point at the left of the figure. The rapid increase in fluorescence when using xylene or naphthalene is ascribed to an energy transfer from tri-*n*-amylborate to the xylene or naphthalene and from these substances ultimately to the solute, since with a 0.1 molar ratio of xylene or naphthalene, most of the high energy (about 90%) is still absorbed in tri-*n*-amylborate. Normally

in a xylene solution, the half-value molar ratios $(C_{\frac{1}{2}})$ of the solutes for energy transfers are about 0.001 and here the half value molar ratio for transfer to xylene or naphthalene is about 5×10^{-2}. It may therefore be concluded that the life-time of the excitation energy in tri-*n*-amylborate is about fifty times shorter than that in xylene if it is assumed that all the other parameters
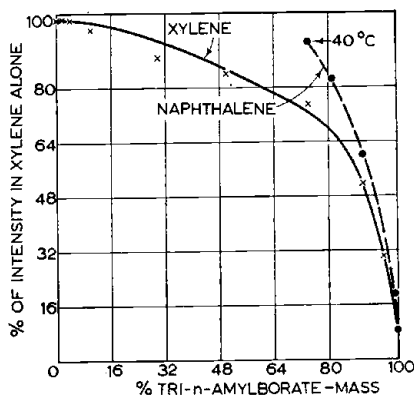

Fig. 3. Gamma-ray fluorescence of 2,5-diphenyloxazole (5 g/l.) in solutions of tri-*n*-amylborate plus naphthalene or plus xylene.

would be the same. That is, of course, only a very crude estimate, since it is not known how much energy is available in tri-*n*-amylborate compared to xylene.

The same procedure used with tri-*n*-amylborate is more or less effective with many other inefficient solvents, and the addition of an intermediate 'solvent' (as the addition of xylene or naphthalene is called) produces considerable high energy induced fluorescence in such solvents. The same procedure is also effective when the solvent is a silicone.

This procedure also helps in solvents which have become less efficient because of the addition of quenching agents. For instance tetralin and dioxane degenerate in effectiveness with time. If naphthalene is added to these solvents when their effectiveness is reduced, the fluorescence increases considerably because naphthalene is less quenched than the forementioned substances Equations (1) and (2) can also be used to explain the action of intermediate 'solvents.' This time they are applied to the process of energy transfer from the inefficient solvent to the intermediate 'solvent'. Now τ_{mlg} and τ_0 represent properties of the solvent from which energy is transferred, in this case, the inefficient one. κ is the only parameter which depends upon the accepting intermediate 'solvent'; the magnitude of κ actually depends on both the transferring and the accepting solvent. It is found that smaller concentrations of naphthalene than of xylene are required to extract energy from all the

inefficient solvents tested up to now. This shows that the cross section for energy transfer to naphthalene is larger than that to xylene.

The transfer process from the intermediate 'solvent' to the solute is also described by equations of the form of (1) and (2). The Q value for this process is gleaned from the curve of fluorescence vs. concentration of the light emitting solute. τ_{mig} and τ_0 now refer to properties of the intermediate 'solvent', and each may depend upon its concentration. For instance τ_{mig}
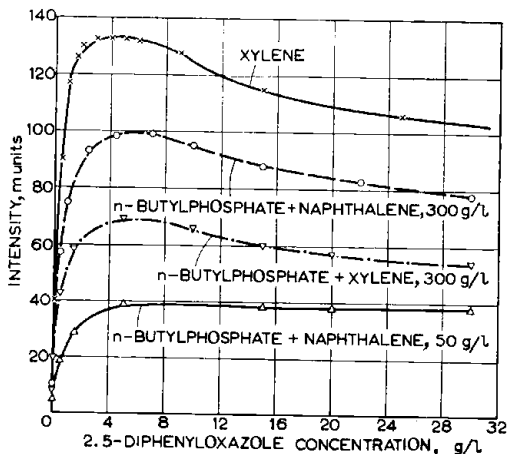

Fig. 4. Gamma-ray induced fluorescence of diphenyloxazole solutions.

(the time required for excitation energy to jump from one intermediate 'solvent' molecule to another) will certainly increase with decreasing concentration of the intermediate 'solvent' since then the average distance between its molecules becomes larger. (See Fig. (4).) Also τ_0 may depend upon intermediate 'solvent' concentration since the lifetime of the excitation energy in this intermediate 'solvent' is known to increase with decreasing concentration (smaller quenching with smaller concentration). Thus both τ_{mig} and τ_0 are expected to increase with decreasing concentrations. At present we cannot predict which increase is greatest although at concentrations normally used for intermediate 'solvents' (mole ratio of about 0.1) one would conjecture that the change in τ_{mig} is greater. It is found that most double solvent combinations (ordinary solvent plus intermediate) have a larger Q than the intermediate solvent when used alone; thus for example energy transfer noticeably begins in xylene at smaller concentrations than in a solution made in an inefficient solvent plus xylene. Figure (4) depicts the fluorescence when *n*-butylphosphate is the main though ineffective solvent, and either xylene or naphthalene is the intermediate 'solvent'. The displacement of C_{max} toward larger concentrations compared to C_{max} in xylene alone is quite marked. It is interpreted as an increase in τ_{mig} due to the longer average distance between the intermediate 'solvent' molecules. It is

also possible that τ_0 is influenced by the presence of the inefficient solvent; experiments particularly of the type to be described in Section V may help clarify the situation.

Another important point in relation to quenching is still to be considered. If a quencher is added to these solutions, the excited solvent molecule or that of the intermediate 'solvent' may be quenched as has been previously discussed. It has been found that the excited naphthalene molecule is less quenched than that of xylene. If one adds small amounts of carbon tetrachloride to a solution of 9,10-diphenylanthracene in xylene, the high energy induced fluorescence is reduced mostly due to quenching of the solvent molecule as ascertained by corresponding experiments using light excitation directly absorbed by the solute (there is also quenching of the solute but much less than the solvent), If enough naphthalene is added to this solution, the energy goes over to the naphthalene from the xylene. The naphthalene acts in this case as an intermediate 'solvent', and it is observed that quenching by carbon tetrachloride is reduced. Naphthalene thus seems to be less exposed to such quenching than xylene. The interesting point is that this low quenching of naphthalene occurs for most kinds of quenchers. For example, p-dioxane is a rather efficient solvent for scintillating solutions. When water is added, the high energy induced fluorescence is found to be low mostly because the excited dioxane molecule is quenched. Addition of naphthalene is found to give fluorescence almost equal to its old intensity. Apparently the naphthalene molecule is not so much quenched by water as are those of dioxane and xylene. Heavy metals also often produce quenching when present in scintillators. Again naphthalene gives fluorescence enhancement. This property of naphthalene of being less quenched than other materials is remarkable. It is of considerable practical significance because it offers a possibility of circumventing many quenching effects, and it is theoretically interesting because of its generality.

This section is concluded with the following summary. It has been shown that energy transfer and quenching of the solvent are probably based on the same type of migration process of the excitation energy: This migration of energy terminates in the transfer process close to a solute molecule whereas in quenching the migration is stopped close to a quenching molecule by means of a non-radiative transition induced by the quencher molecule. The energy transfer process from naphthalene to the solute is about as good as that from the best solvents for liquid scintillators. The reason that quenching of naphthalene is less than that of other effective solvents is not yet known.

V

The fifth subject now to be treated may throw light on this situation from another viewpoint.

Up to now in our discussion of various processes which lead to light emission or which prevent it, knowledge was obtained from light efficiency measurements under different internal conditions of the solution. There is another source of information available; it is the shape of the light intensity vs. time curve of the light flash produced by a single fast particle. Assuming as a first approximation that the excitation process by a fast particle is practically instantaneous and that the time required to transfer the energy from one medium to another is short compared to the lifetime of the emitting molecule, one expects that the flash displays an exponential decay of intensity I with the time constant τ, $I = I_0 e^{-t/\tau}$. I_0, the initial intensity, depends on energy and density of ionization of the incoming particle. The first assumption is reasonable because all charged particles which can traverse a distance of 1 cm in solid or liquid material must have a velocity of the order of magnitude of that of light and as a consequence the time for exciting the bulk of the medium is smaller than 10^{-10} sec; this is small compared to all measured τ. For particles with smaller velocity, the range goes according to a law v^n with $n > 1$ and thus the time of slowing the particle becomes still shorter. The second assumption, that the transfer time is small compared to all known τ is fulfilled as well; it is only indirectly concluded that the time of transfer from the solvent is small compared to the lifetime of the emitting solute molecule. As already pointed out in Section I, there may be some contribution to the light emission from ionization or the formation of free radicals. Their contribution seems to be small, but they would tend to produce a lengthening of the light flash and a decay deviating from an exponential shape. These effects will first be neglected in the discussion. Then the following five familiar formulas are valid:

$$\frac{1}{\tau} = \frac{1}{\tau_e} + \frac{1}{\tau_q} \; ; \; \frac{1}{\tau_e} = P_e; \; \frac{1}{\tau_q} = P_q; \; \xi = \frac{P_e}{P_e + P_q} = \frac{\tau_q}{\tau_e + \tau_q}; \qquad (4)$$

$$\tau_e \sim \int \epsilon \, d\, \nu$$

τ is the time constant actually obtained from measurements of the flash. τ_e is the lifetime of the excited solute molecule if it were to return to the ground state only by means of light emission; its reciprocal P_e is the probability of light emission per unit time. τ_q has a similar significance for quenching (radiationless transition) so that P_q is the probability per unit time of internal quenching, and ξ is the observed efficiency of fluorescence emission under ultraviolet excitation. Measurements of τ (always shorter than either τ_e or τ_q), and ξ thus enable τ_e and τ_q, which are characteristic constants for each solute molecule, to be determined. This determination of τ_e allows an independent check of the relationship between τ_e and the absorption coefficient, given by the last relation in (4). Many fluorescent solutes are found to follow this relationship in order of magnitude; however, there are some exceptions

where this relationship is found not to hold. In these cases, it is assumed that the observed absorption does not produce excitation into the lowest excited state but rather into a higher state having much higher absorption coefficient. The fluorescent emission nevertheless seems to proceed mainly from the lowest state (singlet) which has a rather small absorption coefficient for some molecules and which may be overshadowed by the strong absorption in higher states. Under high energy excitation certainly higher states are also excited, but all observations indicate that most electrons in the higher states go over to the lowest state by means of interactions with the surroundings before light emission occurs.

For the present purpose, the most interesting question, however, is that of the time necessary for energy transfer. Theoretically one obtains the following results: The time variation of the light flash is of the form

$$I = I_0 \left[\exp\left(-\frac{t}{\tau_{tr}} \right) - \exp\left(-\frac{t}{\tau_{S_u}} \right) \right] \tag{5}$$

which essentially describes an exponential rise and decay of the flash. (The previous equation for I is an approximation which considers only the decay assuming an infinitely fast rise.) The rise is in all cases represented by the exponential with the shorter time constant. One of the time constants is the transfer time τ_{tr}, the other τ_{S_u} is the decay time of the fluroescent solute. For the transfer time one can write

$$\frac{1}{\tau_{tr}} = \frac{1}{\tau_0} + \frac{\pi \kappa \, N_{S_u}}{N_{S_o} \, \tau_{\mathrm{mlg}}} \tag{6}$$

(The notation is the same as in equation (2). τ_0 is the lifetime of the excitation energy of the solvent; τ_{mlg} is the time the excitation energy needs to jump from one molecule to the other. κ is a measure of the cross section of energy transfer and N_S / N is the mole ratio of the solute to solvent.) The second term in (6) gives the reduction in lifetime of the solvent due to transfer from the solvent to the solute. Actually τ_{tr} is the lifetime of the excited solvent modified by the transfers to the solute. At large solute concentrations this lifetime is decreased since the excitation energy remains in the solvent molecule for a short time compared to that when no transitions due to transfer to the solute occur. Since this lifetime is the time constant which enters beside τ_{S_u} into equation (5), it is called transfer time. It is indeed the time during which transfer occurs. This period of time depends upon the solute concentration and decreases with increasing concentration. Thus experimentally one can most readily measure τ_{tr} at low concentration. On the other hand at small concentrations the intensity of the light flash is small, and thus measurements cannot so accurately be made as at higher ones. It is convenient to

rewrite equation (6) using $Q \equiv c_{\frac{1}{2}}$ the molar ratio where half the energy is

transferred to the solute. Then equation (6) reads $\dfrac{1}{\tau_{tr}} = \dfrac{1}{\tau_0} \left(1 + \dfrac{c}{c_{\frac{1}{2}}} \right)$ where c

is the solute concentration. This directly shows how τ_{tr} depends upon τ_0 the lifetime of the solvent, upon the Q value of the solvent, and upon the concentration of the solute.

Experiments show that the Q values for a given solvent do not differ greatly among various solutes, and since most practical measurements are performed at concentrations where $c/c_{\frac{1}{2}}$ is about 5, under practical conditions τ_{tr} does not depend strongly upon the solute used. The experimentally observed time constants of organic substances vary, however, over the fairly large range from 2×10^{-9} to about 2×10^{-7} sec for various solutes so that this variation cannot be due to a change of τ_{tr}. A corroboration of this is given by preliminary measurements at low concentrations; they have not revealed any noticeable change in the width of the flash up to now. This is another indication that τ_{tr} is small. The shortest time that has been measured is that of 2,5-diphenyloxazole in xylene and is about 2×10^{-9} sec. This time constant must in part be due to τ_{S_u}. The quantum efficiency of this substance is cf the order of one so that from (4) $\tau_{S_u} \sim \tau_e$. τ_e can be estimated from the absorption spectrum of the solute and is found to be of the order of 10^{-9} sec. Thus the transfer time τ_{tr} and consequently τ_0 cannot be much longer than 10^{-9} sec and is probably shorter.

It is of interest to investigate the variation in τ among solvents and whether any influence of τ_{tr} can be detected. Knowledge of τ_{tr} is also of importance since it would reveal the value of τ_0 and make equation (2) more useful. In that equation, three constants τ_0, τ_{mig} and κ occur, and knowledge of τ_0 would give information about τ_{mig} and κ. The solutions measured so far have shown only very slight indications (if any) that the shape of the flash depends upon the solvent and thus τ_{tr}.

Information about τ_{tr} would also be very important in other respects. Additional quenching processes should shorten the time constant of the transfer process, and the observation of a change in time constants under quenching conditions would also give new information about the quenching process. An illustrative example for using such information will be given in the last subject which will be discussed.

VI

It is well known that under alpha-particle excitation the light emission efficiency is much smaller than for electron excitation. Thus, an electron of 1 MeV is completely absorbed in an anthracene crystal and about 5% of this

energy is transformed to emitted light. For an alpha-particle from Po, from the same amount of energy, 1 MeV, only about 0.5% of the total energy is emitted as light. This decrease by about a factor of 10 in efficiency for alpha-particles compared to fast electrons has been observed for all organic scintillators and is even observed in many inorganic scintillators. In an early state of these investigations, this decrease in emission was already attributed to an additional quenching due to increased density of excitation in the wake of alpha-particle excitation. This idea was given quantitative formulation by Wright and Birks and others; this quenching process was ascribed to a bimolecular reaction between excited molecules. This formulation is not completely satisfactory as will be discussed below.

This quenching by high density of excitation will first be discussed from a qualitative viewpoint. Consider a light flash in a solution which has a time constant τ_{el} when excited by fast electrons. This τ_{el} comes about because of effects of emission time constant τ_e, and any other time constants which are intrinsic to the particular solution being investigated. Under excitation by alpha-particles, an additional quenching occurs in the same solution; one can semi-quantitatively describe this special quenching by a parameter τ_{hd}. The total time constant will be decreased because of this additional quenching.

and the time constant under α excitation, τ_a, is $\dfrac{1}{\tau_a} = \dfrac{1}{\tau_{el}} + \dfrac{1}{\tau_{hd}}$. For

the ratio of the efficiencies under alpha-particles and fast electrons, one obtains

$\dfrac{\xi_a}{\xi_{el}} = \dfrac{\tau_{hd}}{\tau_{el} + \tau_{hd}} = \dfrac{\tau_a}{\tau_{el}}$. This is only an estimation of the relation between

time constants and quenching when there is high density of excitation. The important result is that both should be smaller than the values when the density of excitation is not great. This decrease should depend upon the time constant of the solution under electron excitation for a given τ_{hd}.

An intensive study of scintillating solutions has disclosed that the actual behavior of these solutions under these excitations is quite different from the prediction. The measured ratio of the time constants under alpha-particle and electron excitations is practically one for all measured organic solutions and also other materials instead of being of the order of the efficiency ratio which is about 0.1 for most solutions. This efficiency ratio is thus seen not to depend upon the lifetime τ_{el} at all. A more accurate evaluation of these ratios, using the bimolecular theory of alpha-particle excitation also gives a similar discrepancy. It becomes quite clear that the concept of quenching described above must be incomplete in some respects when there is a high density of excitation. The observation that the light flash time constant is the same for alpha-particles and electron excitation can be interpreted if quenching due to high density of excitation is already finished when actual light emission sets in. The same conclusion can be derived from the result that ξ_a/ξ_e is independent

c

of the lifetime τ_{el} of the solution. The efficiency under electron excitation is essentially determined by τ_e and τ_q. The independence of the ratio ξ_a/ξ_{el} from these parameters can again only mean that quenching because of high density of excitation is a very fast process which essentially is finished when the normal decay (described by τ_e and τ_q) begins.

A theory has been developed which gives results agreeing with the experimental characteristics described here. It is based on the fact that at the initiation of excitation a large density of excitation is produced in a relatively small channel with a diameter of the order of 10^{-6} cm. In this small volume the excitation is so great that the material would have a temperature above 1000°C if all the energy were to be in the form of atomic vibration. In the channel quenching occurs very rapidly; however, the high density of excitation very quickly disappears because of mutual recombinations and dissipation of this energy. This goes on so fast that normal density of excitation is reached long before the main light emission can take place. Only that fraction of the excitation energy which has migrated out of the quenching zone remains available for light emission; the emission occurs with normal time constant.

CONCLUDING REMARKS

In this survey the more important features of the process of energy transfer from the solvent to the solute have been described. Often this discussion had to be of a qualitative nature because accurate quantitative data are not yet available. It is by no means impossible, however, to determine the parameters used in these theories more quantitatively using present methods. Time constant measurements will be of particular value, particularly if differences in time constants for different solutions are studied and if an accuracy is attained which allows determination of the transfer time.

There are quite different methods already in use which I have not had time to mention here, which will help to discriminate between the different processes outlined. For instance similar measurements as in solutions have been carried out in various plastics. By comparing these results with those obtained in liquid solutions, those processes which are based on migration of excitation energy can be separated from those which are based on the diffusion of matter (diffusion of excited molecules). Another idea is that instead of exciting the solvent by high energy, one can excite it also by light of suitable wavelengths. This has the advantage that only the lowest excited state of the solvent can be excited. More careful study can then be made of how the energy is transferred to the solute. Some experiments of this type have been already undertaken and comparison between results obtained using these two types of excitation have disclosed much similarity, but also quantitative differences. They indicate that under high energy excitation higher excited states also participate in the transfer process.