TABLE II

RESONANCE ENERGIES AND CHANGES IN HEAT OF CARBINOL FORMATION FOR COMPOUNDS RELATED TO CRYSTAL VIOLET

Compound	Resonance energies	Heats of carbinol formation referred to crystal violet[a] Theoretical	Experimental
Crystal violet	1.38 (39 kcal./mole)	(0)	(0)
p-Methoxy malachite green	1.27	−0.11	....
Malachite green	1.24	− .14	−0.12
p-Nitro malachite green	1.17	− .21	....

[a] Note that by virtue of the nature of ψ_2 the values in the theoretical column may be quickly computed from the observed 1,2-transition energies. They are simply the negative of the ground state energy differences from CV.

Before concluding this section we need to call attention to a situation which is easy to interpret incorrectly. One might think that if the only difference between pseudo-reactions and bona-fide reactions is in the ambiguity associated with different structure representations, then in some cases there would be no difference at all. For example in paper II we treated benzene under the assumption $n = 2$ (two Kekulé structures) and found no formal ambiguity (no arbitrary constants in S^{-1}). However it must be kept in mind that in all the analysis with the structure representation we deal with an $n \times n$ upper block of an infinitely large matrix E in the Heisenberg representation. The freedom of choice of n, while necessary from the standpoint of fitting structures$_1$ (which may be few in number) to observed levels, gives always an ambiguity in a larger sense. Hence expectation values in the structure representation cannot strictly be interpreted as E values for working out heats of reaction.

This rule has one exception, the case in which the structure representation is the same as the Heisenberg representation (no interactions among the structures, or in structure$_1$ language, no mesomerism). This is the limiting case for which the equivalence relation

$$\text{structures}_1 \approx \text{structures}_2$$

holds perfectly: the domain of applicability of classical valence theory.

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[CONTRIBUTION FROM PHYSICAL CHEMISTRY LABORATORY, OXFORD]

An Experimental Study of the Transfer of Energy of Excitation between Unlike Molecules in Liquid Solutions[1]

BY EDMUND J. BOWEN AND ROBERT LIVINGSTON

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In solutions containing two fluorescent solutes, where the emission spectrum of the first (A) overlaps the absorption spectrum of the second (B), the fluorescence of A is quenched, and the fluorescence of B is sensitized. The intensities of the fluorescence of each component were measured for the following pairs of aromatic hydrocarbons: chloroanthracene–perylene, chloroanthracene–rubrene and cyanoanthracene–rubrene. The transfer of energy of excitation between these compounds is much more efficient than can be accounted for by a process of emission and reabsorption. The data are consistent with the postulate that the non-radiative transfer of energy is a bimolecular interaction between an excited molecule of A and a normal molecule of B. The rate of this interaction is not determined by diffusion, being apparently independent of the viscosity of the solvent and (even in benzene) at least ten-fold faster than a diffusion-controlled process. Furthermore, it is not due to the formation of dimers, as is demonstrated both by the nature of the concentration dependence of the fluorescence and by the validity of Beer's law when applied to the mixed solutions.

The transfer of the energy of electronic excitation between like molecules in liquid solutions results in the depolarization and the self-quenching of the fluorescence of such solutions.[2a,b] Between unlike molecules, the corresponding transfer process results in the quenching of the fluorescence of one species and the sensitization of the fluorescence of the other.[3] Such an energy transfer can be due either to a radiative or to a non-radiative process. The former, commonly referred to as "absorption and remission" or as the "trivial process," is relatively unimportant for most solutions. The non-radiative process, which we shall designate as "classical resonance," has been analyzed theoretically[4,5] (especially by Professor Förster), and its existence has been demonstrated experimentally.[6–9] Of the systems investigated, the chloroanthracene–perylene[9] pair appears to be especially suitable for quantitative study. Measurements of the sensitized fluorescence and concurrent quenching are reported in the present paper for the following pairs of compounds: 1-chloroanthracene and perylene, 9-cyanoanthracene and rubrene, 1-chloroanthracene and rubrene and 9-aldehydoanthracene and rubrene.

Experimental Methods and Materials

The several hydrocarbons were purified chromatographically before use. All the solvents were of Analar grade and

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[1] This work was performed while one of us (RL) was on Sabbatical Furlough from the University of Minnesota, Minneapolis, Minn. and was the recipient of a grant from the Guggenheim Memorial Foundation.

[2] (a) Th. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Göttingen, 1951, pp. 172–180, 230–238; (b) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publ. Inc., New York, N. Y., 1949, pp. 349–352, 378–379.

[3] Th. Förster, ref. 2a, p. 182.

[4] S. Vavilov, *J. Phys.* (*URRS*), **7**, 141 (1943).

[5] Th. Förster, *Ann. Physik*, **2**, 55 (1958).

[6] Th. Förster, *Z. Elektrochem.*, **53**, 93 (1949); *Z. Naturforsch.*, **4a**, 321 (1949).

[7] W. F. Watson and R. Livingston, *J. Chem. Phys.*, **18**, 802 (1950).

[8] L. N. M. Duysens, *Nature*, **168**, 548 (1951).

[9] E. J. Bowen and B. Brockelhurst, *Trans. Faraday Soc.*, **49**, 1131 (1953).

did not fluoresce appreciably at the wave lengths used. The chloroform was freed from added alcohol by washing with water. The extinction coefficients of the hydrocarbon solutions were determined with the aid of a Unicam spectrophotometer. All measurements were made at ambient temperature, 15 to 20°.

The solutions to be examined, deoxygenated by a stream of purified nitrogen, were contained in small glass cuvettes, 1-2 mm. thick, placed in front of the entrance slit of a double monochromator fitted with a photomultiplier at the exit slit.[9] They were illuminated with a condensed beam of monochromatic light (3650 Å.) on the side of the cuvette facing the slit. For solutions of each substance, and of mixtures, at different concentrations, the intensity of the fluorescence of each constituent was obtained from a measurement at a single wave length, which was selected to minimize the effect of reabsorption. For the sensitized fluorescence, the effect of reabsorption was completely negligible. The following formula was used to correct the measured intensity of the fluorescence of the sensitizer

$$I_F\,(\text{cor.}) = \frac{\epsilon_B + r\epsilon_A + (\epsilon'_A + \epsilon'_B)\cos\phi}{\epsilon_B + r\epsilon_A}\,I_F\,(\text{meas.}) \quad (1)$$

where ϵ_A and ϵ_B are the extinction coefficients at $\lambda = 3650$ Å. for the sensitizer and sensitized compounds, respectively, and ϵ'_A and ϵ'_B are those corresponding to the wave length chosen for the measurement of the fluorescence. The quantity r is the ratio of the concentration of the sensitizer to that of the quencher, and ϕ is the angle of incidence of the exciting light on the face of the cuvette. Only that fluorescent light which was (approximately) perpendicular to the front face of the cell passed through the monochromator. Since the collimation and adjustment of the beam of exciting light was imperfect, the correction afforded by equation 1 is only approximate.

Results and their Analysis

The following list of reaction steps (compare reference 7) sets out the elementary processes which affect the observed intensities of fluorescence from mixed and from simple solutions, without reference to any specific mechanism. For example, the rate equations, corresponding to steps 7 through 11, are intentionally expressed in indefinite form, where the $f_i(A,B)$ may be any function of the concentrations of A and B. Steps 4 and 6 may each involve an intermediate, the triplet state. Step 11 represents both the resonance transfer of energy and the process of emission and reabsorption of radiation.

$$h\nu + \mathrm{B} \longrightarrow \mathrm{B}^* \qquad v_1 = \beta J' \qquad (1)$$
$$h\nu + \mathrm{A} \longrightarrow \mathrm{A}^* \qquad v_2 = \alpha J' \qquad (2)$$
$$\mathrm{B}^* \longrightarrow \mathrm{B} + h\nu_f \qquad v_3 = k_3 b = I'_b \qquad (3)$$
$$\mathrm{B}^* \rightarrow \rightarrow \mathrm{B} \qquad v_4 = k_4 b \qquad (4)$$
$$\mathrm{A}^* \longrightarrow \mathrm{A} + h\nu'_f \qquad v_5 = k_5 a = I'_a \qquad (5)$$
$$\mathrm{A}^* \rightarrow \rightarrow \mathrm{A} \qquad v_6 = k_6 a \qquad (6)$$
$$\mathrm{B}^* \xrightarrow{\mathrm{B}} \mathrm{B} \qquad v_7 = f_7(\mathrm{B})b \qquad (7)$$
$$\mathrm{B}^* \xrightarrow{\mathrm{A}} \mathrm{B} \qquad v_8 = f_8(\mathrm{A,B})b \qquad (8)$$
$$\mathrm{A}^* \xrightarrow{\mathrm{A}} \mathrm{A} \qquad v_9 = f_9(\mathrm{A})a \qquad (9)$$
$$\mathrm{A}^* \xrightarrow{\mathrm{B}} \mathrm{A} \qquad v_{10} = f_{10}(\mathrm{A,B})a \qquad (10)$$
$$\mathrm{A}^* + \mathrm{B} \longrightarrow \mathrm{A} + \mathrm{B}^+ \qquad v_{11} = f_{11}(\mathrm{A,B})a \qquad (11)$$

The concentrations of the excited states, [A*] and [B*], are indicated by a and b, respectively. The quantities α and β are the fractions of the monochromatic incident light absorbed by compounds A and B, respectively. To be consistent with the units of the several rate constants, J' is expressed in einsteins per liter per second.

Since the measurements were made with constant intensity of the exciting light, the system was in an exact steady state. Accordingly, $da/dt = db/dt = 0$, and it follows that

$$\beta J' + f_{11}a = (k_3 + k_4 + f_7 + f_8)b \qquad (2)$$

and

$$\alpha J' = (k_5 + k_6 + f_9 + f_{10} + f_{11})a \qquad (3)$$

It will be convenient to introduce the probabilities, w_i, which define the probability that an intermediate, A* or B*, will disappear by undergoing the ith reaction step. For example, the probability that A* will transfer its energy of activation to a molecule B is

$$w_{11} = \frac{f_{11}}{k_5 + k_6 + f_9 + f_{10} + f_{11}} \qquad (4)$$

The intensities of the fluorescent light were measured in arbitrary units for a narrow band of wave lengths and over a very small solid angle. However, these arbitrarily measured intensities I_b are directly proportional to the total emission (in all directions and for all wave lengths), I'_b, in einsteins per liter per second. The constant of proportionality is a function of the wave length used, of the compound and the solvent, and of the geometry of the system, but is independent of the composition of the solution. Therefore

$$I_b/I^0{}_b = I_b'/I^0{}_b' \qquad (5)$$

where I'_b is the intensity of fluorescence from a solution containing A and B at any arbitrary concentrations and $I^0_b{}'$ is the intensity from a second solution having the same concentration of B as the first but containing no A. It follows directly from these definitions and conditions, that

$$\frac{I_a}{I^0{}_a} = \frac{\alpha J'}{J^0{}_a}\,(1 - w_{10} - w_{11}) \qquad (6)$$

and

$$\frac{I_b}{I^0{}_b} = \frac{J'}{J^0{}_b{}'}\,(\beta + \alpha w_{11})(1 - w_8) \qquad (7)$$

In all of the experiments which are reported in this paper the absorption of the exciting light was practically complete; therefore

$$\frac{J'}{J^0{}_a{}'} \cong \frac{J'}{J^0{}_b{}'} \cong 1 \qquad (8)$$

As a first approximation, let it be assumed that $w_8 << 1$. It has been demonstrated empirically[10] that the self-quenching of the fluorescence of these solutions is a diffusional process and obeys a Stern–Volmer type law.

$$\frac{I^0{}_{b,\infty}}{I^0{}_b} = 1 + K_B\,[B] \qquad (9)$$

where $I^0{}_{b,\infty}$ is the limiting, maximum intensity of fluorescence and K_b is the self-quenching constant. The following expression may be obtained by combining equations 7, 8 and 9.

$$w_{11} \cong \frac{\beta}{\alpha}\left[\frac{I_b}{\beta I^0{}_{b,\infty}}\,(1 + K_B\,[B]) - 1\right] \qquad (10)$$

This value of w_{11} includes the process of emission and reabsorption as well as the non-radiative transfer of excitation. If all of the light emitted by A were absorbed by B, the probability of the "trivial"

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[10] E. J. Bowen, *Trans. Faraday Soc.*, **50**, 97 (1954); J. Q. Umberger and V. K. La Mer, THIS JOURNAL, **67**, 1099 (1945).

process would be φ_a, the fluorescent yield of A in the mixed solution. While this is certainly an overcorrection, the true value of the probability, w'_{11}, of the resonance transfer must lie between w_{11} and $w_{11} - \varphi_a$. In principle, it would be possible to approximate much more closely to the true correction by taking into account the steady-state spatial distribution of excited molecules of A as well as ϵ_A and ϵ_B as functions of wave length over the range emitted by A. To the authors, this refinement did not appear to be worth the required effort; particularly, since the correction is relatively unimportant for the chloroanthracene–perylene system. The quantum yield (of A for a mixed solution) ϕ_a, may be evaluated either in terms of I_a (the measured intensity of A corrected for reabsorption) or of w_{11} and the Stern–Volmer constant, K_a.

$$\phi_a = (I_a/\alpha I^0_a)\,\phi^0_{a,\infty} \tag{11}$$

$$\varphi_a \cong \frac{1 - w_{11}}{1 + K_a[A]}\,\phi^0_{a,\infty} \tag{12}$$

It is of primary interest to determine f_{11} as a function of [B]. This can be done in terms of I_b, conveniently by way of the quantity w'_{11}, as follows

$$f_{11} = \frac{w_{11}'(1 + K_a[A])}{(1 - w'_{11} - w_{10})\tau_a\phi^0_{a,\infty}} \tag{13}$$

If w_{10} were much smaller than w_{11}, the quantity $F = w'_{11}(1 + K_a[A])/(1 - w'_{11})$ should be directly proportional to f_{11}. Making the additional approximation that $w'_{11} = w_{11} - \phi_a$, this quantity has been calculated for the measurements which have been made with solutions of chloroanthracene and perylene and the results are summarized in Table I. It is apparent that F is roughly proportional to [B], which is consistent with the hypothesis that $f_{11} = k_{11}[B]$. If this hypothesis be accepted, the data indicate that $w_{10} < 0.1w_{11}$ for benzene solutions, and that $w_{10} \lessgtr 0.3w_{11}$ for chloroform solutions.

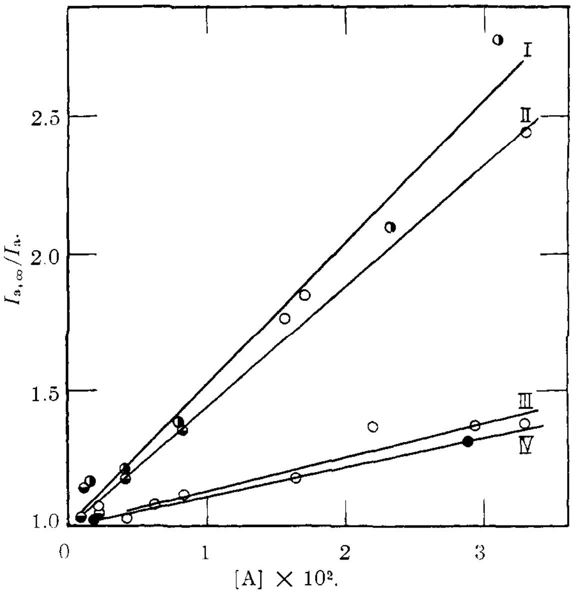

Fig. 1.—The intensity of the fluorescence of λ 4230 Å. as a function of the concentration of chloroanthracene in simple and in mixed solutions: I, chloroform, r = 2.40; benzene, r = 5.1; III, benzene, r = ∞; IV, chloroform, = ∞.

TABLE I

SUMMARY OF THE VALUES OF w_{11}, ETC., FOR 1-CHLOROANTHRACENE–PERYLENE

Wave lengths selected for determination of fluorescence intensities were 5050 and 4740 Å.

Solvent	[B] × 10⁴	$r = \frac{[A]}{[B]}$	w_{11}	$w_{11} - \phi_a$	$\frac{(w_{11} - \phi_a)(1 + K_a[A])}{(1 - w_{11}) + \phi_a}$	$\frac{(w_{11} - \phi_a)(1 + K_a[A])}{[B](1 - w_{11} + \phi_a)}$
C_6H_6	66.0	5.1	0.462	0.429	1.50	160
C_6H_6	33.0	5.1	.309	.264	0.52	130
C_6H_6	16.5	5.1	.242	.181	.235	150
C_6H_6	8.3	5.1	.188	.117	.140	160
C_6H_6	4.1	5.1	.139	.060	.071	170
C_6H_6	54.8	5.35	.442	.392	.875	160
C_6H_6	54.8	2.66	.489	.435	.905	170
C_6H_6	54.8	1.78	.568	.515	.119	220
C_6H_6	54.8	1.32	.583	.529	1.22	220
$CHCl_3$	129.0	2.40	.556	.538	2.05	120
$CHCl_3$	96.8	2.40	.581	.557	1.93	160
$CHCl_3$	64.5	2.40	.534	.505	1.39	180
$CHCl_3$	32.3	2.40	.398	.367	0.69	190
$CHCl_3$	16.1	2.40	.296	.254	.37	220
$CHCl_3$	6.3	2.40	.198	.154	.19	290
Liq. parf.	18.8	1.96	.258	.202	.25	140
Liq. parf.	9.4	1.96	.173	.108	.12	130

The same definitions and postulates which were used in the derivation of equation 13, may be employed to obtain a relation between $f_{10} + f_{11}$ and the partially quenched fluorescence of A.

$$\begin{aligned} \frac{\alpha I^0_{a,\infty}}{I_a} &= \frac{I_{a,\infty}}{I_a} \\ &= 1 + \frac{f_9 + f_{10} + f_{11}}{k_5 + k_6} \qquad (14) \\ &= 1 + K_a[A] + (f_{10} + f_{11})\tau_a\phi^0_{a,\infty} \end{aligned}$$

This relation has been tested with the measured fluorescent intensities at λ 4230 Å. for the chloroanthracene–perylene systems, by plotting $I_{a,\infty}/I_b$ against [A] on Fig. 1. Within the rather broad limits of experimental precision, the several sets of points correspond to straight lines passing through the origin. The data determining the numbered lines were obtained with the following systems: I, mixed solution in chloroform, r = 2.40; II, mixed solution in benzene, r = 5.0; III and IV chloroanthracene (alone) in benzene and chloroform, respectively. The slopes of lines III and IV are equal to the Stern–Volmer constant, while the slopes of lines I and II are equal to $rK_a + (k_{10} + k_{11})\,\tau_a\phi^0_{a,\infty}$.

The several rate coefficients, k_i, can be calculated in terms of the product $k_{11}\tau_a\phi_{a,\infty}$, the self-quenching constants, the natural lives, and the maximum fluorescent yields. The last two of these quantities have been calculated and tabulated[10] for a number of aromatic hydrocarbons by Dr. E. J. Bowen. Tentative values for these rate coefficients and related quantities are listed in Table II.

The half-lives, τ_a and τ_b, have been calculated[10] from measured extinction coefficients of solutions in benzene. While the effect, of changing the sol-

TABLE II

SUMMARY OF THE RATE CONSTANTS AND RELATED QUANTITIES

A B Solvent	Chloroanthracene perylene benzene	Chloroanthracene perylene chloroform	Chloroanthracene perylene liquid paraffin	Chloroanthracene rubrene benzene	Cyanoanthracene rubrene benzene
τ_b, sec.	6.9×10^{-9}	(6.9×10^{-9})	(6.9×10^{-9})	2.1×10^{-8}	2.1×10^{-8}
$k_3 = \tau^{-1}$, sec.$^{-1}$	1.45×10^8	(1.45×10^8)	(1.45×10^8)	4.8×10^7	4.8×10^7
$\phi_{b,\infty}$	0.96	0.88	(0.96)	1.00	1.00
$k_4 = (\phi_{b,\infty}^{0-1} - 1)k_3$, sec.$^{-1}$	5.9×10^6	(2.0×10^7)	(5.9×10^6)	$\gtrless 2 \times 10^6$	$\lessgtr 2 \times 10^6$
τ_a, sec.	1.2×10^{-8}	(1.2×10^{-8})	(1.2×10^{-8})	1.2×10^{-8}	1.1×10^{-8}
$k_5 = \tau_a^{-1}$, sec.$^{-1}$	8.3×10^7	(8.3×10^7)	(8.3×10^7)	8.3×10^7	9.0×10^7
$\phi^0{}_{,\infty}$	0.085	0.065	(0.085)	0.085	0.48
$k_6 = (\phi_{a,\infty}^{0-1} - 1)k_5$, sec.$^{-1}$	8.9×10^8	(1.19×10^9)	(8.9×10^8)	8.9×10^8	9.7×10^7
K_b, mole^{-1}	34.0	32.5	<30	25	25
$k_7 = K_b(k_3 + k_4)$, mole^{-1} sec.$^{-1}$	5.1×10^9	(5.4×10^9)	$(<5 \times 10^9)$	1.2×10^9	1.2×10^9
K_a, mole^{-1}	12.2	10.5	<3	12.2	124
$k_9 = K_a(k_5 + k_6)$, mole^{-1} sec.$^{-1}$	1.2×10^{10}	(1.3×10^{10})	$(<3 \times 10^9)$	1.2×10^{10}	2.3×10^9
$k_{11}{}^a$ mole^{-1} sec.$^{-1}$	1.7×10^{11}	(2.5×10^{11})	(1.4×10^{11})	1.5×10^{11}(?)	3.0×10^{11}
k_{11},^{b} mole^{-1} sec.$^{-1}$	1.6×10^{11}	(1.4×10^{11})	..........^{c}	....	2.5×10^{11}
$[A]_{1/2}{}^m$	6.2×10^{-3}	(5.4×10^{-3})	(7.0×10^{-3})	7.1×10^{-3}(?)	6.9×10^{-4}
$\bar{R}_{1/2}$, Å.	41	(42)	(39)	38(?)	84

[a] Values based upon equation 13 and measurements of I_b. [b] Values based upon equation 14 and measurements of I_a. [c] The solvent was appreciably fluorescent at shorter wave lengths, which made measurements at λ4230 Å. unreliable.

vent, upon the half-life is small, some slight uncertainty is introduced in the calculated quantities (k_3, k_4, k_5, k_6, k_7, k_9 and k_{11}) by the assumption, that the lifetimes are the same in all three solvents. The maximum fluorescent yields were not measured for liquid paraffin solutions; however, comparison of the intensities, at λ4230 for A and λ5050 Å. for B, indicates that no great error is introduced by assuming that the yields in liquid paraffin and benzene are identical. Due to the small solubilities of the hydrocarbons in liquid paraffin, only limiting (maximum) values of the self-quenching constants could be determined. In calculating k_{11}, it was assumed that self-quenching is negligible in liquid paraffin solutions. It was assumed, in the calculation of all of the values of k_{11}, that k_8 and k_{10} were negligibly small. The data indicate that neither k_8 nor k_{10} are comparable to k_{11}, but it is entirely possible that they may be as great as k_7 or k_9. If it be assumed that k_{10} equals k_9, the calculated values of k_{11} are increased by about 20%. The measurements made with chloroform solutions, are better represented by the parameters, $k_{11} = 3.2 \times 10^{11}$ and $k_{10} = 1.0 \times 10^{11}$, than they are by those given in Table II. However, the data are not sufficiently precise to justify a definite choice between these pairs of values.

In terms of the preceding empirical analysis, the probability of energy transfer, w_{11}, should be one-half when the concentrations of the sensitizer and sensitized compound are each equal to

$$[A]_{1/2} = (\tau_a\phi_a{}^0{}_{,\infty}k_{11} - K_a)^{-1}m$$

The corresponding average separation, $\bar{R}_{1/2}$, between unlike molecules, can be calculated from the relation[6]

$$\bar{R}_{1/2} = 7.35[A]_{1/2}^{-1/3}\ \text{Å}.$$

These quantities are listed in the last two rows of Table II.

As a test of the agreement between the observations and their theoretical interpretation, the calculations have been reversed. Values of $I_b/I^0{}_b$, have been computed by introducing the numerical constants of Table II into the following equation, which can be derived from the basic postulates and approximations

$$\frac{I_b}{I^0{}_{b,\infty}} = \frac{1 - (1 - w_{11}')\alpha}{1 + K_b[B]} + \frac{\phi^0{}_{a,\infty}\,\alpha(1 - w_{11}')}{(1 + K_b[B])(1 + K_a[A])} \tag{15}$$

where

$$1 - w'_{11} = \frac{1 + K_a[A]}{1 + K_a[A] + \tau_a\phi^0{}_{a,\infty}k_{11}[B]} \tag{16}$$

The individual values of I_b were reproducible within 5 or 10%. However, additional uncertainties are introduced by possible variations in the temperature and concentrations and in the completeness of the removal of dissolved oxygen. Systematic errors might be introduced in evaluat-

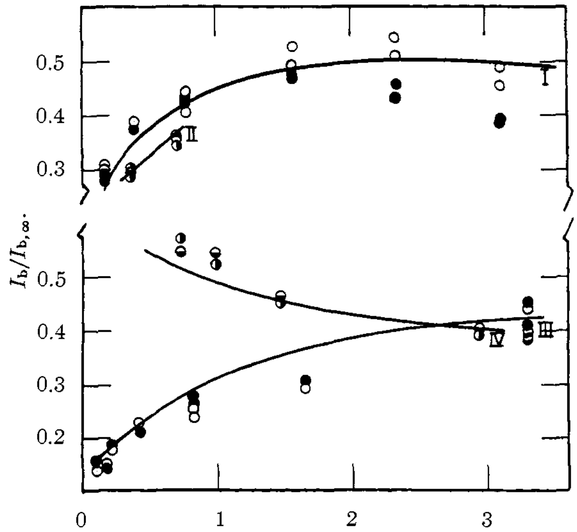

Fig. 2.—The probability of energy transfer, w_{11}, as a function of the concentration of chloroanthracene: I, chloroform, r = 2.40; II, liquid paraffin, r = 3.68; III, benzene, r = 5.1; IV, benzene, [B] = 0.0055 m; points ◒ ◒, ● ●, λ 4740 Å; ◑◑, ○ ○, λ 5050 Å.

ing $I^0_{b,\infty}$, K_a, K_b and the extinction coefficients and by the use of the rough approximation in correcting for the trivial process. Therefore, an over-all error of 15 to 20% in the individual values should not be surprising. For measurements made with benzene and liquid paraffin solutions, the general agreement between theory and experiments is within the expected limits. For chloroform solutions there appears to be systematic deviation at higher concentrations, which could be eliminated if it were postulated that $3k_{10} \simeq k_{11}$.

A similar study was made of benzene solutions of rubrene and 9-cyanoanthracene and of rubrene and 1-chloroanthracene. While the efficiency of exchange, w_{11}, is very great for the rubrene–9-cyanoanthracene pair, its general behavior is similar to that of perylene and 1-chloroanthracene. In particular, f_{11} appears to be directly proportional to [B], for both systems. This is not true for the system rubrene–1-chloroanthracene. Either the measurements on the latter system were subject to some unsuspected systematic error, or else, for it, f_{11} is more nearly a quadratic than a linear function of [B]. Accordingly, the corresponding value of k_{11} (Table II) is of doubtful significance.

A few measurements were made of the fluorescence of benzene solutions containing rubrene and 9-aldehydoanthracene. The latter compound is non-fluorescent; ϕ being less than 0.001. However, assuming the validity of the mirror image law, the emission spectrum of 9-aldehydoanthracene should strongly overlap the absorption spectrum of rubrene, so that sensitized fluorescence seemed at least possible. Within the limits of our measurements, 9-aldehydoanthracene does not sensitize the fluorescence of rubrene, but instead acts as a fairly efficient quencher. Its Stern–Volmer quenching constant is approximately 58 mole^{-1}; which corresponds to k_8 equal to 2×10^9 liter mole^{-1} sec.$^{-1}$.

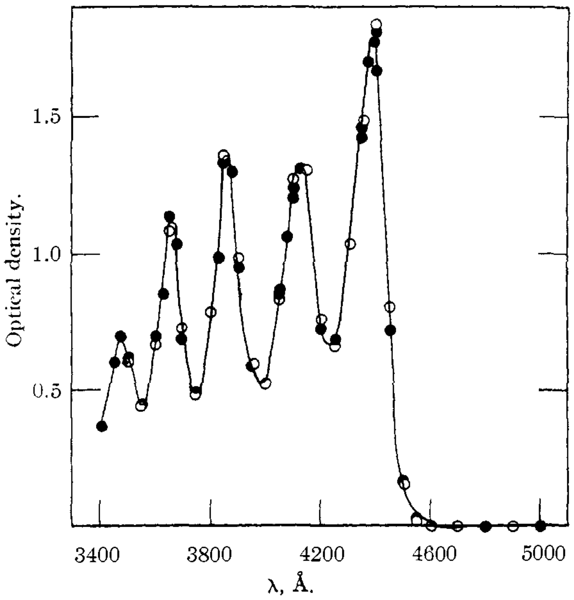

Fig. 3.—Absorption spectra for mixtures of chloroanthracene and perylene, $r = 1.97$; O, molarity of chloroanthracene $= 1.16 \times 10^{-2}$ (optical density values multiplied by 3.14); ●, molarity of chloroanthracene $= 1.16 \times 10^{-4}$.

The specific reaction rate of a diffusion-controlled bimolecular reaction is represented approximately by equation 17[10]

$$k_D = \frac{8RT}{3 \times 10^3 \eta} \text{ mole}^{-1} \text{ sec.}^{-1} \qquad (17)$$

where η is the coefficient of viscosity. The values of k_D corresponding to benzene and chloroform, at 20°, are 1.0×10^{10} and 1.1×10^{10} mole^{-1} sec.$^{-1}$, respectively. The empirical values, Table II, of the rate constants, corresponding to self-quenching, do not exceed these predicted maxima. In contrast to this, the rate constants, k_{11}, exceed the calculated maxima by factors ranging from 15 to 30. The difference is even more striking for the system chloroanthracene–perylene in liquid paraffin. The empirical value of k_{11} for this system is a thousand-fold greater than 1×10^8 mole^{-1} sec., the value of k_D for $\eta = 0.5$ poise. It follows that energy exchange between unlike arylhydrocarbons is not a diffusional process although the self-quenching of these hydrocarbon solutions appears to be the result of simple bimolecular reactions. This latter conclusion should not be generalized, since the self-quenching of chlorophyll solutions is a quadratic rather than a linear function of concentration[7] and is independent of the viscosity of the solvent.[11]

It has been suggested that the transfer of energy of excitation between unlike molecules is the result of the formation of mixed, stable dimers. The data reported here do not support this view.

The simplest form of this mixed-dimer hypothesis can be stated as follows. The monomers, A and B, are in equilibrium with the dimer, AB. The molar extinction coefficient of AB is the sum of the coefficients of A and B. All photons which are absorbed by dimers result in the excitation of the B component of the molecule. The fluorescent spectrum and quantum yield of B are unaffected by its dimerization with A. No transfer of energy occurs from excited A to either B or AB. These postulates lead to the following equation, in which K is the equilibrium constant for dimerization.

$$w_{11} = \frac{(1+r)b + K^{-1}}{2rb}\left[1 - \sqrt{1 - \frac{4rb^2}{([1+r]b + K^{-1})^2}}\right] \qquad (18)$$

Equation 18 is incompatible with the data of Table I.

As an additional test of the mixed-dimer hypothesis, the absorption spectrum of a benzene solution containing 0.0116 *m* chloroanthracene and 0.0058 *m* perylene was measured, using a cuvette 0.0032 cm. thick. After a one hundred-fold dilution, the absorption spectrum was redetermined, using a 1.00 cm. cuvette. As Fig. 3 demonstrates, the two spectra are identical within the limits of error, although energy transfer occurs efficiently in the concentrated solution and is negligible for the dilute. Beer's law also holds when solutions of each component are mixed.

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[11] S. Weil, Doctoral thesis, Univ. of Minn., 1952.