Theoretical expressions describing long-range singlet energy transfer have been derived by Förster.[11] For the case of weak coupling, R_0, the distance in centimeters at which the transfer rate equals the normal decay rate of the excited donor, is given by eq 8 where ϕ_D is the fluorescence

$$R_0 = \left(\frac{(8.79 \times 10^{-25})K^2\phi_D}{n^4}\int_0^\infty f_D(\tilde{\nu})\varepsilon_A(\tilde{\nu})\frac{d\tilde{\nu}}{\tilde{\nu}^4}\right)^{1/6} \quad (8)$$

quantum yield of the donor, K^2 is an orientation factor (taken as $^2/_3$ for random distribution), n is the index of refraction of the solvent, f_D is the donor fluorescence spectrum normalized to unity, and ε_A is the acceptor molar decadic extinction coefficient. The integral in eq 8 is large when there is good spectral overlap between donor fluorescence and acceptor absorption. Figure 1 shows the spectral overlap between *trans*-stilbene fluorescence and azulene absorption. The calculated value of R_0 in benzene is 16 Å.[17] The experimental value of R_0 in ångströms is given approximately by eq 9.[18,19] Substitution

$$R_0 = 7.35\left(\frac{k_1}{k_F + k_4}\right)^{1/3} \quad (9)$$

of the rate constant ratio from Table I in eq 9 gives 18 Å for R_0, in excellent agreement with the theoretical value.[21]

Our results show that eq 1 is responsible for the azulene effect on the direct photoisomerization of the stilbenes and that the triplet mechanism does not obtain.

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(16) We have observed such an effect with *p*-bromostilbene for which the triplet mechanism provides the minor path (20–35%) for the isomerization at 30°.
(17) We thank Dr. A. A. Lamola for the evaluation of the integral in eq 8.
(18) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 101.
(19) Dr. A. A. Lamola has informed us that a treatment which attempts to be exact gives 6.32 instead of 7.35 in eq 9.[20] With this substitution a value of 15 Å is calculated for the experimental R_0.
(20) R. Povinelli, Ph.D. Thesis, University of Notre Dame, 1964.
(21) Derivation of eq 8 is based on the assumption that R_0 is large compared to molecular dimensions. The close correspondence between the theoretical and experimental values of R_0 is interesting, since this assumption is marginal in this case.[22]
(22) D. W. Ellis and B. S. Solomon, *J. Chem. Phys.*, **46**, 3497 (1967).
(23) National Institutes of Health Predoctoral Research Fellow, 1965–present.

Book Reviews

Thermodynamics of Steady States. By RALPH J. TYKODI, Associate Professor of Chemistry, Southeastern Massachusetts Technological Institute. The Macmillan Co., 866 Third Ave., New York, N. Y. 1967. xvii + 217 pp. 16 × 24 cm. $10.95.

It is well known that scientists react strongly to thermodynamics. To some, its inner logic and economy of principle make it an esthetically satisfying and powerful tool; to others, it is merely useful and dull. Some thermodynamicists regard their subject as well founded on a few simple and obvious axioms; others (like myself) feel that the subject is not really complete without reference to its molecular foundation in statistical mechanics. Textbooks clearly reflect this difference in attitude.

Nonequilibrium thermodynamics seems to provoke much the same reactions. For those who feel most comfortable when statistical mechanical foundations are emphasized, the classic book by DeGroot and Mazur is still the best text on this subject. Those who prefer the axiomatic approach may find Tykodi's book appealing.

The author states his basic premises at the outset. In addition to the laws of ordinary thermodynamics, these can be paraphrased as follows: (1) nonequilibrium steady states can be maintained experimentally; (2) a nonequilibrium system can be divided into terminal parts and gradients, much in the way that electric networks can be treated as black boxes with inputs and outputs; (3) steady-state situations are governed by the principle of minimum entropy production; and (4) Onsager's reciprocal relations are valid. (Statistical mechanics tells us that premises 3 and 4 are correct for *linear* nonequilibrium processes. For nonlinear processes, it is still not clear what the appropriate generalizations are.)

From these principles, Tykodi analyzes many experimentally interesting situations involving steady flow of heat, radiant energy, electricity, and matter. Some examples are the various thermoelectric effects, thermal diffusion, concentration cells, etc. As in conventional thermodynamics, the language and notation are elaborate. A number of problems or exercises are presented; some are concerned with numbers, while others are in the fine old tradition of thermodynamic texts: "Derive Eqs. (8.15) and (8.16) from Eqs. (8.12) and (8.13)."

In conclusion, I feel that this book accomplishes successfully what the author claims in his preface: "This book does for the class of non-equilibrium situations and steady state processes what any good book on ordinary thermodynamics does for equilibrium situations; it develops a series of relations of interest in their own right; it helps the experimentalist plan his experiments efficiently by making use of the necessary interconnections among experimentally determined quantities; it provides the experimenter with some consistency checks on his measurements; and it yields equations interrelating macroscopic quantities—equations that are of use to engineers and that serve as guides for more detailed kinetic theory or statistical mechanical analysis of the phenomena." If you are satisfied with this minimal (though important) view of the subject, Tykodi's book will serve. If you want to know what is really going on in your nonequilibrium system, where the molecules are and what they are doing, you will have to go elsewhere.

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Amino Acid Determination. Methods and Techniques. By S. BLACKBURN, Wool Industries Research Association, Leeds, England. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 10016. 1968. xi + 271 pp. 16 × 23 cm. $12.50.

A student recently asked me to suggest a book which would give him a summary of the various parameters that have to be considered in the separation of amino acids by ion-exchange chromatography. Blackburn's monograph had just arrived and met this test fairly well.

The history and the current practice of the quantitative separation of amino acids on sulfonated polystyrene resins are covered in considerable detail. Ion exchange, although the major topic, is only one of the subjects surveyed by the author; the book describes and compares most of the current approaches to amino acid analysis.

Although in many respects the text is as up to date as can be expected in a field in which improvements are constantly being introduced, there are some exceptions. The discussion on interference from ninhydrin-positive peptides in acid hydrolysates (p 16) is based primarily upon a 1954 paper for which the hydrolyses were performed at 105°; it could have been added that at the recommended temperature of 110° interference is not a practical problem after 20 hr. The summary on the reduction of proteins for determination of half-cystine as carboxymethylcysteine (p 130) should have been extended from the use of thioglycolic acid and sodium borohydride to the procedures with mercaptoethanol. Contemporary tables and maps which would indicate the approximate positions of elution of the some 100 amino acids and related compounds that have been studied on ion-exchange columns would have been useful to many readers. The main theme of the text, as mentioned on page 133, is the analysis of purified proteins; this emphasis has probably determined the limited treatment of some topics.

Analyses of physiological fluids and foodstuffs are summarized briefly. Sections are included on colorimetric and spectrophotometric methods for specific amino acids and the separations of amino acid derivatives. There are chapters on paper chromatography, high-voltage paper electrophoresis, mass spectrometry, and gas chromatography. The potentialities of all of these procedures are thoughtfully appraised in a concluding chapter on future methods.

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