

$\phi_{ST} = 0.4^9$) was chosen as a sensitizer,¹⁰ probably capable of transferring its triplet energy to both I and II. Irradiation of the I-II-naphthalene system (26°) with 2537-Å light gave only phenol and at a rate *at least 30 times faster than that of an identical but unsensitized run*. It is important to note that this enormous rate enhancement was observed under conditions where the II:I ratio is *ca.* 70:30¹ and must be a consequence of energy transfer to both species. Phenol is thus the product of triplet II as well as I and possibly also of singlet I. It follows that III, shown earlier to come from II, is the product of a singlet process and that intersystem crossing of singlet II must be extremely inefficient. Data obtained with other sensitizers are not quite as decisive as those described but are in complete accord with conclusions drawn.

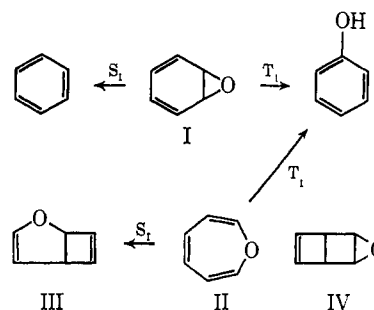
Dewar benzene oxide (IV) is known to give phenol and I-II thermally as well as photochemically¹¹ and therefore warrants consideration as a possible intermediate in transformations of I-II. Repeated attempts

(9) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(10) Photosensitization experiments were performed in matched quartz cells. The two were identical in *all* respects, except for the deletion of sensitizer from the reference cell. Comparisons are drawn only between the two sets of data from such a pair. Except where noted, solutions (pentane) were 0.1 *M* in substrate and 1.0 *M* in sensitizer.

(11) E. E. van Tamelen and D. Carty, *J. Am. Chem. Soc.*, **89**, 3922 (1967).

to detect intermediates such as IV have not been successful. Until direct evidence for the involvement of IV is in hand, we will assume that the photoconversion of IV to phenol proceeds *via* I-II.



Corroborative data from quantum yield measurements are presently being obtained, and it is expected that we will be able to refine the scheme outlined above and comment in the full paper on the likelihood of hot ground-state reactions.^{5,12}

(12) This is considered unlikely, because collisional deactivation of vibrationally excited molecules is normally very fast in solution. The possibility cannot be dismissed in this case, however, because the thermal formation of phenol is quite facile.

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Additions and Corrections

Alkylcobaloximes and Their Relation to Alkylcobalamins [*J. Am. Chem. Soc.*, **88**, 3738 (1966)]. By G. N. SCHRAUZER and R. J. WINDGASSEN. Department of Chemistry, University of California, San Diego, California.

In Table II the values for the O-H··O signals in the ¹H nmr spectra of several methylcobaloximes were erroneously quoted 500 cps too far upfield. The last column of Table II should read:

Axial component	O-H··O
H ₂ O	-8.93
py	-8.93
P(OCH ₃) ₃	-8.83
P(<i>n</i> -C ₄ H ₉) ₃	-8.18
P(C ₆ H ₅) ₃	-8.20

On page 3741, column 1, the third line from the bottom should read: O-H··O protons at -0.6.

Aromatic Azapentalenes. III. 1,3a,6,6a-Tetraazapentalenes [*J. Am. Chem. Soc.*, **89**, 2633 (1967)]. By J. C. KAUER and R. A. CARBONI. Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

On page 2633, in the last line of the second column, "ferric" should be corrected to "ferrous."

Nucleophilic Displacements at Sulfur. III. The Exchange of Oxygen-18 between Sodium Thiosulfate-¹⁸O and Water [*J. Am. Chem. Soc.*, **89**, 3379 (1967)]. By WILLIAM A. PRYOR and UMBERTO TONELLATO. Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

The mechanism postulated for this exchange, eq 7 and 9, predicts a negative slope when log *k* is plotted *vs.* $\mu^{1/2}$. The data of Table II and Figure 2 show that the slope is near zero. Two possible explanations can be suggested for this discrepancy. First, these data are all at ionic strengths greater than 0.1, and the Debye-Hückel limiting law may well not apply here. Second, these data of necessity were determined in unbuffered solutions, and the effect of ionic strength on the dissociation of water should be taken into account. If this is done, the data can be recalculated to show a slight negative slope. The exact value of the slope cannot be determined without a knowledge of α and K_w at 80°, but it is doubtful if these data in unbuffered solutions are accurate enough to justify a detailed treatment. In either case, the mechanistic arguments of the paper stand unchanged.

The following typographical errors should also be corrected. The pH of run 1 in Table I should be 5.39 (not 5.93). The third line of footnote 15 should read: "plus 0.01 *M* sulfite..." (not 0.1 *M*). The page number of ref 23 should be 300 (not 30). The sulfate species at the bottom of the first column on p 3386 should have one more negative charge on oxygen; that is, it should be H_3SO_6^- .

Mean Activity Coefficient of Polyelectrolytes in the Ternary System Water–Sodium Polyacrylate–Sodium Chloride [*J. Am. Chem. Soc.*, **89**, 3697 (1967)]. By TSUNEO OKUBO, NORIO ISE, and FUMIO MATSUI. Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

On page 3702, in the caption of Figure 9, the clause, "X, osmometrically observed by Takahashi, *et al.*"¹⁹ should be deleted. The figure "3" on the ordinate of Figure 7 should be deleted.

The Analysis of AA'BB' Nuclear Magnetic Resonance Spectra by Weak Double Irradiation. Application to

Two Isomeric Cyclobutane Derivatives [*J. Am. Chem. Soc.*, **89**, 3953 (1967)]. By E. LUSTIG, E. P. RAGELIS, N. DUY, and J. A. FERETTI. The Food and Drug Administration, Washington, D. C. 20204.

In Table III, *cis*, column *d*, the third number from the top should read "(−19.19)," rather than "(+19.19)."

The Role of Neighboring Groups in Replacement Reactions. XXVII. 5-Methoxyl Participation in Some Solvolysis Reactions [*J. Am. Chem. Soc.*, **89**, 3991 (1967)]. By EVAN L. ALLRED and S. WINSTEIN. Department of Chemistry, University of California, Los Angeles, California, and Department of Chemistry, University of Utah, Salt Lake City, Utah.

In this and the following papers in this series (pages 3998, 4008, and 4012), the term "5-Methoxyl" in the title ("6-Methoxyl" in the paper on page 4012) should be replaced by the expression "MeO-5" ("MeO-6"). The MeO-5 and MeO-6 symbols follow previous usage, where the 5 and 6 indicate the size of the ring formed.

Book Reviews

Thermodynamics and Statistical Mechanics. By A. H. WILSON, F.R.S. Cambridge University Press, 32 East 57 St., New York, N. Y. 1966. xv + 495 pp. 12 × 23 cm. \$2.95.

Professor Wilson's monograph first appeared in a hard-covered edition about 10 years ago. During the intervening time it has enjoyed a splendid career. In keeping with a growing trend to reissue older but still useful books at lower prices, it has now reappeared in a paperback edition at about one-third of the original price. Although the quality of the paper is somewhat less than in the original edition, it is still quite satisfactory; the excellent format is unchanged from the earlier printing, the original plates having been used.

The book begins with three chapters on thermodynamics, developed along classical lines. Next follows a chapter on the axiomatic approach, following the lines of Carathéodory. Chapter 5 introduces statistical mechanics, beginning at once with a formulation in terms of stationary quantum states, and arriving at classical statistical mechanics only later *via* a limiting process. Chapter 6 considers several elementary applications of statistical mechanics. Chapter 7 deals with the third law of thermodynamics, the discussion leaning heavily upon statistical mechanics. The remaining chapters may be classed as applications. The subjects discussed include (not in order) heterogeneous equilibria, gas mixtures and chemical reactions, solutions, electrolyte solutions, electrochemical systems, imperfect gases, solids, and electric and magnetic phenomena.

The book was written primarily from the point of view of the theoretical physicist. Because of this, the interplay between statistical mechanics and thermodynamics is quite strong. In addition, the assumption is made that the reader at least conceptually understands some areas best known by physicists. As an example of this, the development of statistical mechanics presupposes a knowledge of the concepts of quantum mechanics. As another example, the chapter on electric and magnetic phenomena presupposes a knowledge of some areas of electromagnetism.

This book is pitched at a rather sophisticated level, and as such is not useful for a first introduction to the material. For the graduate student of theoretical physics, the presuppositions stated above will afford no difficulty, since he generally already will have studied the subjects mentioned when he reaches the level of Professor Wilson's book, or at any rate he will be studying them simultaneously.

For the graduate physical chemist undergoing modern training, this remark usually should also apply with respect to quantum mechanics, although possibly not to electromagnetism and some other less crucial material. Except for a few chapters on applications, such lack of knowledge should not be a problem. For other chemists and for chemical engineers, the situation would probably be more difficult, and this book would be less likely to be the ideal choice for them.

The greatest use for this book probably is as a reference. All of us from time to time find it necessary to reintroduce ourselves to material previously known but somewhat forgotten as a result of disuse. Within the fields that it covers, it provides convenient, clear, detailed, and analytic discussions of the material. With this in mind, it well can take a useful position on the bookshelves of many people. These remarks are particularly valid for the theoretical physicist and physical chemist, but are also not without application to others. In particular, the last seven chapters, on applications, contain a wealth of information on the subjects discussed, always presented in a well-written manner. With few exceptions, the validity of this material has not changed in the decade since it was written. At the current low price, it is certainly well worth owning.

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