

exhibits two very broad bands centered at about 5400 and 6700 Å. In water the compound is rapidly oxidized to rhodizonate ion,  $C_6O_6^{-2}$ .

The magnetic properties of  $C_6O_6^{-4}$  are of especial interest in connection with its electronic structure. Simple LCAO molecular orbital calculations<sup>3</sup> predict a biradical nature for  $C_6O_6^{-4}$ . However, measurements by the Gouy method show that  $K_4C_6O_6$  is diamagnetic. The compound may be one in which electron correlation effects, neglected in the simple MO approach, operate to prevent the degeneracy. Similar arguments have been used to predict a non-degenerate ground state for cyclobutadiene.<sup>4</sup> A complete treatment of  $C_6O_6^{-4}$ , including configuration interaction, would present a formidable theoretical problem.

Pure  $K_4C_6O_6$  gives no electron spin resonance signal, but the compound is rapidly oxidized upon

The rhodizonate anion in the crystalline salts  $Na_2C_6O_6$  and  $K_2C_6O_6$  appears also to have a non-planar or otherwise distorted geometrical form.

(3) D. L. Powell, M. Ito and R. West, unpublished work.

(4) D. P. Craig, *Proc. Roy. Soc. (London)*, **A202**, 498 (1950); cf. A. D. Liehr, *Z. physik. Chem., N. F.*, **9**, 338 (1956).

exposure to air, with the development of a strong esr signal. Incomplete oxidation of  $K_4C_6O_6$  under ether also converts it to a strongly paramagnetic solid, green in color, with a single electron spin resonance near  $g = 2.003$ . A similar green salt may be obtained instead of  $K_4C_6O_6$  in the preparation described above if a small amount of oxygen is present. Further oxidation converts the green salt to potassium rhodizonate, but samples stored in the absence of oxygen maintain their radical nature almost undiminished for several months. It has not yet proved feasible to prepare this radical substance in pure form, but observations so far are consistent with the hypothesis that the green salt may contain the tripotassium salt of the aromatic radical-trianion,  $C_6O_6^{-3}$ .

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## BOOK REVIEWS

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**Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest.** By H. GOBIND KHORANA, Institute for Enzyme Research, University of Wisconsin. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1961. ix + 141 pp. 15.5 × 23.5 cm. Price, \$5.25.

This volume derives from a series of lectures given at the Rockefeller Institute in 1959, but is up-dated with many references into 1961. It naturally emphasizes the author's interests but is an essential for those interested in nucleotide and polynucleotide syntheses. The first twelve-page chapter is a survey of phosphate compounds of importance in biological reactions and is certainly worthy of attention by any graduate student.

SLOAN-KETTERING DIVISION OF  
CORNELL UNIVERSITY MEDICAL COLLEGE  
NEW YORK 21, N. Y.                      GEORGE BOSWORTH BROWN

**The Electrical Double Layer Around a Spherical Colloid Particle. Computation of the Potential, Charge Density, and Free Energy of the Electrical Double Layer Around a Spherical Colloid Particle.** By A. L. LOEB, Associate Professor of Electrical Engineering, Massachusetts Institute of Technology, J. TH. G. OVERBEEK, Professor of Physical Chemistry, University of Utrecht, and P. H. WIERSEMA, van't Hoff Laboratory, University of Utrecht. The M.I.T. Press, Massachusetts Institute of Technology, Cambridge, Massachusetts. 1961. 375 pp. 18.5 × 26 cm. Price, \$10.00.

This book reports the numerical integration of the Poisson-Boltzmann equation for spherical colloidal particles in electrolytic solution. Results are presented in terms of reduced (*i.e.*, dimensionless) quantities. First,  $y$  (reduced electrostatic potential) is calculated as a function of  $x$  (reduced reciprocal distance from center of particle) with  $y_0$  and  $q_0 = 1/x_0$  ( $x_0$  and  $y_0$  are values of  $x$  and  $y$  at particle surface, outer Helmholtz plane, or slipping plane depending on application) as parameters.  $I_+$  and  $I_-$  ( $x^2/4$  times excess charge due to cation and anion outside of a sphere of reduced radius  $1/x$  centered on the particle center) and

the reduced double layer free energy  $F$  are calculated from the previously calculated dependence of reduced potential on reduced reciprocal distance. Tabular results are given for 1-1, 2-1, 3-1, 1-2 and 1-3 electrolytes; data for other symmetric electrolytes (2-2, 3-3 etc.) can be calculated readily from results for 1-1 electrolytes.

Part I of the book (pp. 1-42) describes the method of integration, including transformations of variables to dimensionless groups, an outline of the numerical integration method selected for IBM-704 computer programming, and an outline of methods for transforming tabular results (all in dimensionless groups) into quantities of physical interest. Results of the present calculation are compared with those of the Debye-Hückel approximate treatment and the flat plate double layer. Empirical analytical forms representing data for  $I$  and  $F$  to within 26% and 20%, respectively, are also given. Part I contains 28 tables.

Part II (pp. 46-372) presents the dependence of  $y$ ,  $I_+$ ,  $I_-$ , and  $F$  on  $x$  with  $y_0$  and  $q_0$  as parameters in tabular form for 1-1, 2-1, 3-1, 1-2 and 1-3 electrolytes. Computations for 1-1 electrolytes are particularly extensive (pp. 46-208); results for  $q_0 = 0.1$ , for example, are presented for the range  $0.3 \leq x \leq 10.0$  in units of 0.1 for  $1 \leq y_0 \leq 16$  with increments of 1 from 1-10, 2 from 10 to 16; this is repeated with reduced ranges of  $x$  for  $q_0 = 0.2, 0.5, 1.0, 2.0, 5.0, 10$  and  $20$ . For values of  $x$  smaller than those tabulated the Debye-Hückel approximation is adequate. The authors state that numerical interpolation between tabulated results will generate results accurate to 0.1% if carefully done; linear interpolation between values of  $x$  for fixed  $q_0$  and  $y_0$  appears generally possible to within 1%, but interpolation between different values of  $q_0$  and  $y_0$  will require more refined interpolation involving, for example, ratios of tabulated quantities to approximate or empirical analytical representations of them.

This is a specialist's book concerned principally with numerical results. These results appear to be carefully obtained, and to reflect solutions of the Poisson-Boltzmann equation of adequate precision and detail covering a wide range of parameters. The authors point out that the Debye-Hückel approximation to the Poisson-Boltzmann equation is only valid if  $Zey/kT \ll 1$ . Applicability of