yond its original meaning, but the author makes allowance for this. Another custom, and one which now is perhaps less justified, is the attributing of the dipole moments of molecules such as water to bond polarity, thus ignoring the important role of the lone pair electrons.

In Chapter 4 the author introduces the Lewis concept of acids and bases. Most of the chapter consists of a well-organized discussion of the kinds of chemical species which behave as Lewis acids.

The last two chapters are devoted to base and acid displacement and addition reactions. A wide range of topics is treated, with the main concern being the nucleophilic and electrophilic substitution and addition reactions, and the acid- and base-catalyzed elimination reactions, of organic chemistry. A thorough and up-to-date introduction to these topics is presented. Relative rates of electrophilic substitution in aromatic systems are, for example, quite properly considered from the standpoint of the stability of the transition state, and only then is the older "electron availability" approach mentioned as yielding "largely equivalent" predictions.

The book is written in a quite readable style. It should be of particular interest to students who plan to take courses in organic chemistry. The book should also serve as a good starting point for those chemists whose academic training occurred in earlier years, and who wish to learn something about the more recent theoretical principles of ionic reactions at the covalent bond.

The concept of a series of supplementary monographs such as this one is a relatively new approach to the first-year college chemistry course, and one which is being adopted by more than one publisher. Offsetting the increased cost to the student of a textbook plus several monographs is the obvious advantage of having each topic discussed by an authority in the particular field. This approach will undoubtedly make available some fresh and timely new text material.

DEPARTMENT OF CHEMISTRY
KNOX COLLEGE
GALESBURG, ILLINOIS
HARRY J. NEUMILLER, JR.

Contributions to the Thermodynamics of Surfaces. By J. J. BIKERMAN. Published by the Author, 20-c-223, Massachusetts Institute of Technology, Cambridge 39, Massachusetts, 1961. 76 pp. 13.5 × 21.5 cm.

Professor Bikerman here presents a collection of our papers which, as he states in his preface, he "did not succeed to place. . . in suitable scientific journals." They are entitled "Two Notes on the Thermodynamics of Capillarity. I. The Surface Free Energy, II. The Adsorption Equation," "The Nature of Surface Pressure," "Theory of Young's Equation of Wetting" and "Experiments on Young's Equation of Wetting."

In this reviewer's opinion each article in this collection contains errors or garblings of concepts serious enough to make their publication difficulties with reputable scientific journals understandable. The book may serve a purpose in causing readers to re-examine critically some of the classical concepts in surface thermodynamics, but if the re-examination is careful the classical concepts will survive it.

For example, the first paper attributes to Gibbsian thermodynamics the hypothesis that if the interfacial layer "say 100 angstroms thick" were separated from the bulk phases and then "homogenized" no free energy change would result. This is absurd, and is not implied by Gibbsian thermodynamics; Eq. 5 preceding it is allegedly based on Gibbsian thermodynamics, but is incorrect in omitting a surface tension term (so is Eq. 13), and is not to be found in Gibbs[1] work (it apparently resulted from an incorrect integration of an equation for dE (Gibbs Eq. 477), applicable (and so stated by Gibbs) to a system with fixed boundaries.

The paper on surface pressure asserts that the ideal spreading pressure equation $\pi = nkT$ is incorrect and that the derivation based on Henry's law limiting adsorption equations is fallacious since with finite solubilities no equilibrium spreading pressure could exist. This latter statement is strictly true, but in the same sense one could claim that application of equilibrium thermodynamics to gases in cylinders is invalid, since no cylinder material can be found for which the gas diffusion constant is zero. (A statistical derivation of the equation $\pi = nkT$ for "insoluble" mobile monolayers is given by Fowler and Guggenheim[2]). According to Bikerman, the correct equation is $\pi = NS(\gamma_0 - \gamma_2 - \gamma_{12})$, where S is the area occupied by one molecule. An equation such as this might be justified for condensed monolayers ($NS \approx 1$); to demonstrate its validity, Bikerman presents experimental data for siloxanes on various host liquids, but at monolayer concentrations 10^{-7} g./cc. (*i.e.*, approximately a condensed film 10 Å. thick). The experiments, in short, were not relevant to the ideal monolayer model.

A recent paper by Johnson[3] gives a clear discussion of Young's equation; this equation depends on a tension balance (or virtual work argument) applied to *the drop periphery*, and Bikerman's examples suggest that this point is not clear to him. For a deformable solid (such solids were used by Bikerman in the fourth paper to illustrate his ideas experimentally) arguments similar to those used in obtaining Neuman's triangle are applicable; the validity of this treatment has been demonstrated, for the case in which the solid is replaced by mercury and all tensions are subject to direct measurement, in a recent paper by Smolders.[4]

CHEMISTRY DEPARTMENT
IOWA STATE UNIVERSITY
AMES, IOWA
ROBERT S. HANSEN

---

(1) J. W. Gibbs, "Collected Works," Yale University Press, New Haven, Conn., 1948, Vol. 1, pp. 219ff.

(2) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," University Press, Cambridge, England, 1956, p. 424, Eq. 1003, 4.

(3) R. E. Johnson, Jr., *J. Phys. Chem.*, **63**, 1655 (1959).

(4) C. A. Smolders, *Rec. trav. chim.*, **80**, 699 (1961).