

the original date of publication of which is not given (it happens to be 1962). It starts from the wrong title—the French “Physique Electronique des Solides” fits the contents far better than the English title, which is misleading, because the book has very little to do with electronics, as will become apparent.

The book has chapters on quantum mechanics, Fermi-Dirac statistics, electron theory of metals, semiconductors and magnetism. I find it difficult to see what the author had intended in writing this book with this subject matter. It is not, it cannot be for its volume, a rigorous treatment. Yet there is a lot of mathematics, or rather algebra, which makes the grasping of the physical significance of various arguments very difficult. Also the choice of the particular topics, which are very selective and yet lacking in real depth, is difficult to justify.

The book has to be judged by its English title, so let it be said that the following omissions are grave for a book under this title published so recently.

No mention is made of Hall effect—this may be understood if one bears in mind that despite a long argument about holes, the author falls into the familiar trap of equating (negative mass, negative charge) with (positive mass, positive charge). This would have given him the wrong sign of Hall effect for holes. Only silicon and germanium appear to exist as semiconductor materials. Lifetime of excess carriers is dismissed in a few lines. There is no discussion of the dependence of mobility on any parameters. No mention is made of surfaces and their effects. Unrationalized MKS units are used. Treatment of p-n junctions is rather confusing. Only alloyed transistors are mentioned. No references are given whatsoever. Perhaps the only acceptable chapter is the last one on magnetism.

I cannot recommend this book for teaching of solid state electronics, not even under its French title of “Electronic Physics of Solids”. A. K. JONSCHER

## CURRENTS IN POLAROGRAPHY

### Catalytic and Kinetic Waves in Polarography

By Stal' G. Mairanovskii. Translated from the Russian by Bela M. Fabuss. Translation edited by Petr Zuman. Pp. xiv + 352. (Plenum Press: New York, 1968.) \$19.50.

THE electrochemical reduction of organic compounds in aqueous solution frequently involves hydrogen ions and this makes possible the use of such methods as polarography for a study of the protolytic reactions of organic materials. In the general case of an electrode process, the overall reaction can be broken down into a number of steps not all of which involve electron transfer. This is also true of organic electro-reductions. The stages occurring on or near the electrode surface differ from similar steps occurring in the bulk of the solution because of the effects of the electric field in the double layer and of the adsorption of the participating compounds. In order to interpret the polarograms successfully, it is necessary to understand the relations between these factors and the rate of the reaction as measured by the current.

These effects are responsible for the production of the so-called kinetic and catalytic currents in polarography. Although these are discussed briefly in a number of texts, such as Kolthoff and Lingane's classic *Polarography*, as far as I am aware, there has been no comprehensive and authoritative book to cover them. This new work by Mairanovskii must be considered from this point of view.

The author gives numerous examples of electrode reactions occurring at the dropping mercury electrode which are complicated by the chemical stages, and the experimental methods of examination are briefly outlined. The parts of the book devoted to the calculation of the kinetic parameters are the most important. The detailed derivations of key equations are not usually

given because they can be found in the original references, but the assumptions made in the derivations are clearly stated. The effects of adsorption, antecedent reactions, the double-layer structure and changes in the solution brought about by the presence of organic solvents are discussed in detail. One of the stated objectives of this book is to determine the reactivity of organic compounds in terms of the polarographic half-wave potential. This is not clearly achieved, and the discussion could have been emphasized more in order to draw these conclusions together more closely.

This apart, the author has succeeded in producing a well written and authoritative work which should become the standard reference within the field.

I have a number of minor criticisms. The index is inadequate, and a list of commonly used symbols and their meanings would have been useful. There is a small number of misprints, but within the context they are so obvious as to be unimportant. P. A. BROOK

## CHEMICAL REACTIONS

### Linear Free Relationships

By P. R. Wells. Pp. vii + 116. (Academic Press: London and New York, November 1968.) 37s 6d; \$5.95.

WHEN the logarithms of the rate (or equilibrium) constants for one reaction series are linearly related to those for a second reaction series which is subjected to the same variations in structure or reaction conditions, a linear free energy relationship is said to hold; this is because the logarithm of a rate (or equilibrium) constant is proportional to the free energy of activation (or equilibrium) for the reaction. Hammett first made the observation in 1937 that the equation  $\log(k/k_0) = \sigma\rho$  (where  $\sigma$  depends only on the substituent and  $\rho$  only on the reaction type) correlates reasonably successfully the reactivities of a large number of *meta* and *para*-substituted benzenoid compounds such as benzoic esters. Since then, there have been two developments: first, Hammett's equation has been submitted to various modifications and elaborations, with the emphasis on the correlation of substituent effects; and second, linear free energy relationships concerned with changes in the reaction medium and with changes in the nature of the reagent (as opposed to the organic substrate) have been reported.

It is with these relationships that Wells's book is concerned. It cannot have been an easy book to write, because the field is a somewhat confused one. This is partly because a large number of slightly different free energy relationships is needed even to correlate substituent effects; thus, the substituent constants ( $\sigma_0$ ) required for the correlation of the reactivities of substituted phenylacetic acids and their derivatives are different from those for electrophilic substitutions in benzenoid compounds ( $\sigma^+$ ), a fact which makes chemical as well as statistical sense (eight different types of  $\sigma$ -constant are listed in the index). And it is partly because the application of linear free energy relationships has often been abused in the chemical literature; correlations, often crude, have been observed and erroneous conclusions have been drawn from them. Moreover, the statistical validity or otherwise of much that has been done has been ignored; for example, it is clear that the elaboration of a particular linear free energy relationship by the introduction of an extra parameter must inevitably improve the fit, and great care must be taken in drawing conclusions in such cases.

Wells has picked his way carefully and sensibly through the wide-ranging literature; his account is not exhaustive, but the salient features are all included. Even so, the book is not easy to read and makes for a sort of chemical indigestion; but this can be attributed in large measure to the nature of the subject. Certainly the book provides a