

Editors

Prof. Dr. Gaston Berthier
Université de Paris
Institut de Biologie
Physico-Chimique
Fondation Edmond de Rothschild
13, rue Pierre et Marie Curie
F-75005 Paris

Prof. Dr. Michael Literae var
Department of Chere
The University of Texas
Austin, Texas 78712/USA

Prof. Dr. Hanns Fischer
Physikalisch-Chemisches Institut
der Universität Zürich
Rämistr. 76
CH-8001 Zürich

Prof. Kenichi Fukui
Kyoto University
Dept. of Hydrocarbon Chemistry
Kyoto/Japan

Prof. Dr. George G. Hall
Department of Mathematics
The University of Nottingham
University Park
Nottingham NG7 2RD/Great Britain

Prof. Dr. Hermann Hartmann
Akademie der Wissenschaften
und der Literatur zu Mainz
Geschwister-Scholl-Straße 2
D-6500 Mainz

Prof. Dr. Hans H. Jaffé
Department of Chemistry
University of Cincinnati
Cincinnati, Ohio 45221/USA

Prof. Joshua Jortner
Institute of Chemistry
Tel-Aviv University
61390 Ramat-Aviv
Tel-Aviv/Israel

Prof. Dr. Werner Kutzelnigg
Lehrstuhl für Theoretische Chemie
der Universität Bochum
Postfach 102148
D-4630 Bochum 1

Prof. Dr. Klaus Ruedenberg
Department of Chemistry
Iowa State University
Ames, Iowa 50010/USA

Prof. Dr. Eolo Scrocco
Via Garibaldi 88
I-00153 Roma

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Edited by G. Berthier M. J. S. Dewar H. Fischer
K. Fukui G. G. Hall H. Hartmann H. H. Jaffé J. Jortner
W. Kutzelnigg K. Ruedenberg E. Scrocco

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G. A. Martynov
R. R. Salem

Electrical Double Layer
at a
Metal-dilute Electrolyte
Solution Interface



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Authors

G. A. Martynov

Institute of Physical Chemistry of the USSR Academy of Sciences
Leninsky Prospect 31, Moscow, USSR

R. R. Salem

D.I. Mendeleev Chemical and Technological Institute
Miussakaya square 9, Moscow, USSR

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Preface

Most of the properties of a metal-electrolyte interface, even the specific nature of an electrode reaction, proneness of a metal to corrosion, etc., are primarily determined by the electrical double layer (EDL) at this boundary. It is therefore no surprise that for the last, at least, one hundred years intense attention should have been centered on EDL. So much of material has been gathered to date that we are easily lost in this maze of information. A substantial part of the attempts to systematize these facts is made at present within the framework of thermodynamics. Such a confined approach is undoubtedly inadequate. The Gouy-Chapman theory and the Stern-Grahame model of the dense part of EDL developed 40-70 years ago, tailored appropriately to suit the occasion, inevitably underlie any description of EDL. This route is rather too narrow to explain all the facts at our disposal. A dire necessity has thus arisen for widening the principles of the microscopic theory. This is precisely the objective of our monograph. Furthermore, we shall dwell at length on the comparison of the theory with experiment: without such a comparative analysis, any theory, however elegant it may be, is just an empty drum.

The monograph is divided into two large sections. Section I is devoted to the ionic part of EDL whose charge is formed by the ions in the solution and Section II, to the electronic part whose charge is produced by the electrons in the metal (see Fig. 1). Such a bifurcation is motivated by two factors. First, the behaviour of ions in a solution obeys the laws of the statistical mechanics of classical systems (indeed, massive ions are typically classical objects), whereas the behaviour of electrons in a metal is governed by the laws of quantum mechanics. The theory of the ionic part does not, as a consequence, run parallel to the theory of the electronic part. Second, while writing these sections we set diverse tasks before ourselves. Surely, there is no uncertainty whatever about the validity of the Gouy-Chapman concepts on the structure of the ionic part. How then to embed these ideas into a more sophisticated general statistical theory - an indispensable tool for describing the more subtle effects left out in the Gouy-Chapman theory? That is the crux of the problem here. As for the electronic part, the situation is otherwise. The presently prevailing Stern-Grahame theory of the molecular capacitor, in which no heed is paid to the individual properties of a metal, as will be shown below, needs to be supplanted by the theory of the electronic capacitor, whose parameters depend largely on the properties of the metal.

Thus, the determinative point at issue here is to justify on sound argumentation the choice of one model in preference to the other. This guideline has naturally moulded in its own way the presentation in Section II.

Prior to taking up the subject proper, let us put forward a plea in defence of our outlook.

Unfortunately, we cannot claim to have been impassive to all the viewpoints known in the literature. We do not hide our bias toward a general physical theory that could interpret as many more experimental data on EDL as possible with as many lesser assumptions as permissible. Therefore, the speculations and hypotheses (though, sometimes, quite novel and fruitful) concerning special problems (for instance, the structure of EDL in a particular metal) have been left untouched. Possibly, this is a minus of the monograph. We are nevertheless of the opinion that a survey of special theories would have diverted the reader from the goal set forth without throwing any new light on the area.

Finally, a word about the structure of the monograph. Each chapter is prefaced with a protracted introduction purposefully, so that a reader wishing to gain a bird's eyeview of the topic may restrict himself only to these introductions.

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