Consultant Editor
A. D. Buckingham

Volume 6

Electrochemistry

Edited by **J. O'M. Bockris**

MTP International Review of Science

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Edited by **J. O'M. Bockris**
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MTP International Review of Science

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Publisher's Note

The MTP International Review of Science is an important new venture in scientific publishing, which we present in association with MTP Medical and Technical Publishing Co. Ltd. and University Park Press, Baltimore. The basic concept of the Review is to provide regular authoritative reviews of entire disciplines. We are starting with chemistry because the problems of literature survey are probably more acute in this subject than in any other. As a matter of policy, the authorship of the MTP Review of Chemistry is international and distinguished; the subject coverage is extensive, systematic and critical; and most important of all, new issues of the Review will be published every two years.

In the MTP Review of Chemistry (Series One), Inorganic, Physical and Organic Chemistry are comprehensively reviewed in 33 text volumes and 3 index volumes, details of which are shown opposite. In general, the reviews cover the period 1967 to 1971. In 1974, it is planned to issue the MTP Review of Chemistry (Series Two), consisting of a similar set of volumes covering the period 1971 to 1973. Series Three is planned for 1976, and so on.

The MTP Review of Chemistry has been conceived within a carefully organised editorial framework. The over-all plan was drawn up, and the volume editors were appointed, by three consultant editors. In turn, each volume editor planned the coverage of his field and appointed authors to write on subjects which were within the area of their own research experience. No geographical restriction was imposed. Hence, the 300 or so contributions to the MTP Review of Chemistry come from many countries of the world and provide an authoritative account of progress in chemistry.

To facilitate rapid production, individual volumes do not have an index. Instead, each chapter has been prefaced with a detailed list of contents, and an index to the 13 volumes of the MTP Review of Physical Chemistry (Series One) will appear, as a separate volume, after publication of the final volume. Similar arrangements will apply to the MTP Review of Organic Chemistry (Series One) and to subsequent series.

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INDEX VOLUME

Physical Chemistry
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Consultant Editor
A. D. Buckingham

Consultant Editor's Note

The MTP International Review of Science is designed to provide a comprehensive, critical and continuing survey of progress in research. The difficult problem of keeping up with advances on a reasonably broad front makes the idea of the Review especially appealing, and I was grateful to be given the opportunity of helping to plan it.

This particular 13-volume section is concerned with Physical Chemistry, Chemical Crystallography and Analytical Chemistry. The subdivision of Physical Chemistry adopted is not completely conventional, but it has been designed to reflect current research trends and it is hoped that it will appeal to the reader. Each volume has been edited by a distinguished chemist and has been written by a team of authoritative scientists. Each author has assessed and interpreted research progress in a specialised topic in terms of his own experience. I believe that their efforts have produced very useful and timely accounts of progress in these branches of chemistry, and that the volumes will make a valuable contribution towards the solution of our problem of keeping abreast of progress in research.

It is my pleasure to thank all those who have collaborated in making this venture possible – the volume editors, the chapter authors and the publishers.

Cambridge A. D. Buckingham

Preface

The principal change which has come about in theoretical chemistry during the last generation—say from about 1930—is that the macroscopic, thermodynamic treatment of systems has given place to their microscopic treatment in terms of statistical and quantum mechanics.

This change was delayed by about 20 years in electrochemistry. One reason was the dominance of Nernst's theory of electrochemical cells—a bastion of the chemical texts of the 1930s and 1940s. The slow weaning had sociological consequences: it contributed to delays in the development of the direct conversion of chemical to electrical energy by electrochemical means (thence to pollution-free transportation).

Meanwhile, there has been a great trend among electrochemical researchers to turn towards the study of electrode processes, and solution aspects have become more a part of the physical chemistry of solutions.

During the last few years, research in electrode processes has brought attention to the interdisciplinary aspects of the field, while the environmental needs of the near future have been a stimulus to a broad development of the electrochemical principles which underlie surface aspects of chemistry, engineering, metallurgy, and biology.

This present situation is the background for choice of the chapters for this first volume on electrochemistry. One chapter concerns very fundamental theory, two describe the basic principles of powerful tools, and three consist of electrochemical discussions of processes in metallurgy, materials science, and biology.

Pennsylvania J. O'M. Bockris

Contents

1

The Quantum Mechanical Model for Electronic Charge Transfer at Interfaces

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1.1 INTRODUCTION

The object of this paper is to give a critical discussion of the present state of the theory of charge transfer at the electrode–electrolyte interface.

1.2 COURSE OF DEVELOPMENT OF THE QUANTUM THEORY OF ELECTRODE PROCESSES

Two distinct paths in the development of the theory of electrode processes are apparent. These may be called the 'thermal' and 'electrostatic' (dielectric continuum) models according to the type of activation involved.

In the thermal view, the vibrational quantum level of the reactant is considered to be distributed in response to the thermal and electrostatic (e.g. ion–dipole) interactions of the ion with the surrounding solvent. In the electrostatic model, the energy changes in the ion leading to electron transfer arise from long-range electrostatic interaction. In practice, the solutions to the equations of the theory are worked out in continuum terms. A brief outline of the development of each of these theories follows.

1.2.1 Development of the thermal model

At an early stage in the development of the quantum theory, Gurney[1] indicated the essential condition for radiationless quantum mechanical electron transfer between metal and solution. An essential aspect of this mechanism is a quantum state in the electron-accepting or -donating ion with the same total energy as that of the typical electron (or hole) in the electrode. This energy corresponds closely to the Fermi level of the metal. The general concept is shown in Figure 1.1. The total energy of the ground electronic state of the proton depends not only upon the vibrational state of the $H_2O—H^+$ bonds *but is affected by the interaction of the* H_3O^+ *ion with its environment*, i.e. the solvation energy of the hydroxonium ion. Part of this energy is continuum in character so that the *total* energy of the electron quantum state in the ion has continuum levels.

In the Gurney model, the product formed by the transfer of an electron to a proton was considered to be a hydrogen atom in water rather than a hydrogen atom bonded to the electrode. Calculation of the heat of activation on this basis gave values that were too high[2]. *For this (trivial) reason*, Gurney's theory was not further considered for about three decades, and was widely misunderstood as it was assumed[2,3] to involve slow *electron* transfer as a rate-

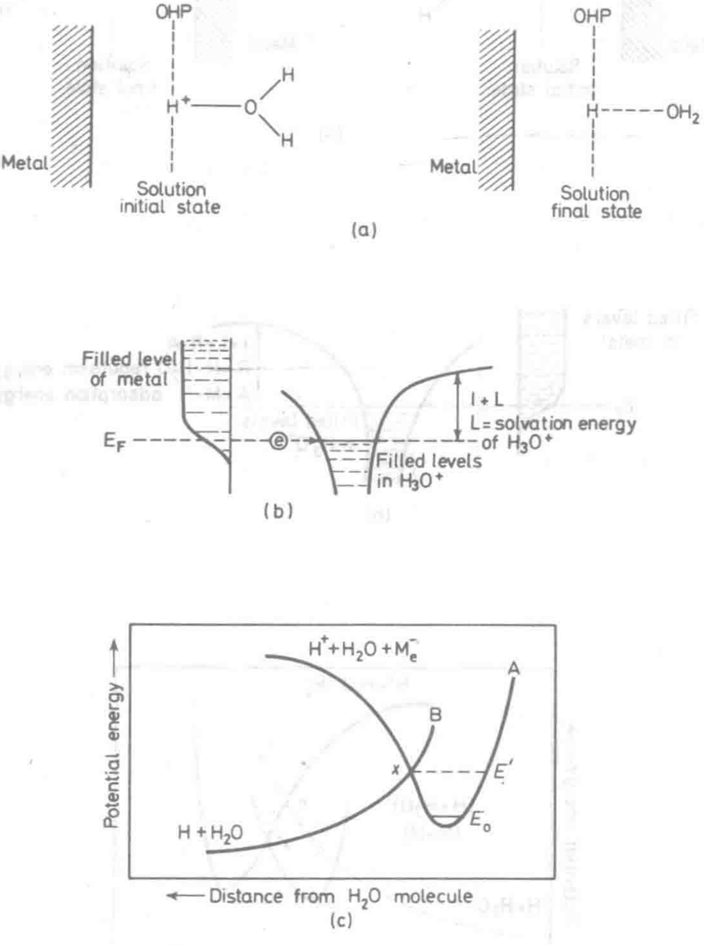

Figure 1.1 The Gurney model for h.e.r.: (a) the model, (b) barrier for electron tunnelling, (c) potential energy profile

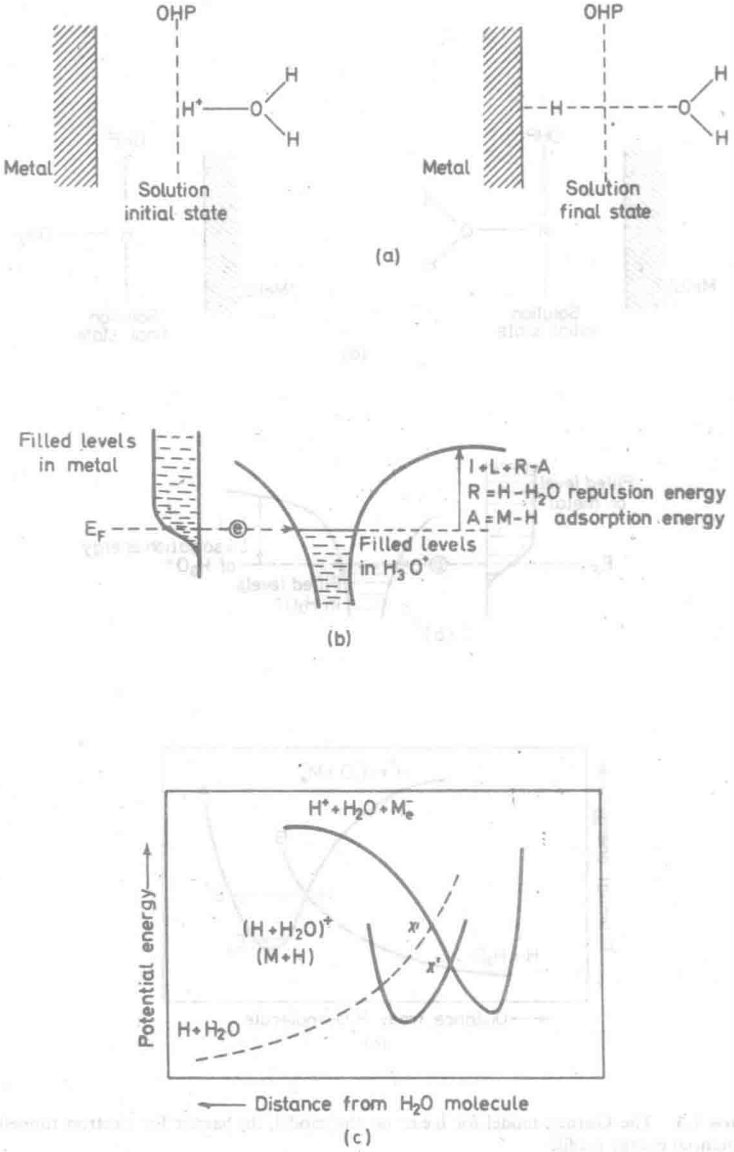

Figure 1.2 The Butler model for h.e.r.: (a) the model, (b) barrier for electron tunnelling, (c) potential energy profile

determining step, whereas in fact it comprises slow rearrangement of the solvation shell (i.e. of the bonds in the solvated H_3O^+ ion) with quantum mechanical electron transfer.

Butler[4] modified Gurney's mechanism to take into account bonding* (chemisorption) of the product hydrogen atoms (in $H_3O^+ + e \rightarrow H_{ads}$) to the metal (Figure 1.2). He considered the potential energy curve for the initial state to be represented by a Morse curve for the H^+—H_2O bond, the solvation energy of the H_3O^+ ion being considered part of the potential energy of the ground state of the proton. The potential energy curve for the final state was taken to be represented by the Morse curve for the metal–hydrogen bond together with a H—H_2O repulsive term.

Parsons and Bockris[5] developed Butler's extension of the Gurney theory, with the assumption that the probability of electron transfer to the proton was unity at the crossing point at the col of the potential energy surfaces (cf. Butler[4]). They were able to separate, from the electrochemical potentials of the metal–ion system, a numerical value corresponding to the charge-dependent part of the potential difference. They made a rough numerical estimate of the rate of the proton discharge reaction under adiabatic electron transfer conditions, and showed that the modified Gurney mechanism was consistent with the measured rates so long as the M—H bond strength was at least 50 kcal mol^{-1}.

Parsons and Bockris[5], in their calculations of one-dimensional potential-energy profiles, used Morse curves for reactants and products. It is important to note that they used the *total* energy of H_3O^+ (i.e. *including the energy of solvation of* H_3O^+ *by the surrounding solvent*) to calculate the potential energy-distance relations by which the activational rearrangement of the solvent was determined.

The same kind of model was used in several applications by Conway and Bockris[6–8]. In each case, the mechanism always implicitly involves adiabatic quantum mechanical electron transfer, and consists of a *bond rearrangement*, with *solvent rearrangement* (represented by the variation of a part of the heat of solvation† of the discharging ion) being involved as some portion of the activation energy.

Although one-dimensional calculations of this type were relatively crude, they allowed the effect of *changes* in quantities (for example, in metal deposition, the bonding of an ion to a planar site in a metal, or to a kink site)

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*Horiuti and Polanyi[3] had (previously) pointed out the effect upon the reaction rate of the metal–hydrogen bond. Their paper did not consider the quantum mechanical aspects of electron transfer, as did the prior paper of Gurney[1] or the immediately subsequent paper of Butler[4]. Butler's model tock both Gurneyian quantum mechanical transfer, and the effect of M—H bond strength changes into account. We do not think that a primary place should be given (in the historical development) to Horiuti and Polanyi's[3] paper, because its level of sophistication was so much less than those of Gurney[1] and of Butler[4].

†The heat of solvation considered was the total interaction energy of the ion with the solvent, i.e. the ion-dipole part, together with the continuum Born energy. As the ion oscillates within its solvation shell, some of the ion–dipole interaction is distance-dependent and hence varies with the movement of the central ion. The energies concerned with some of these movements, for example, that of the ion with the second layer of water molecules, are as low as of the order of kT. Consequently, the potential-energy distance curve for the energy of the ion has a continuum character.

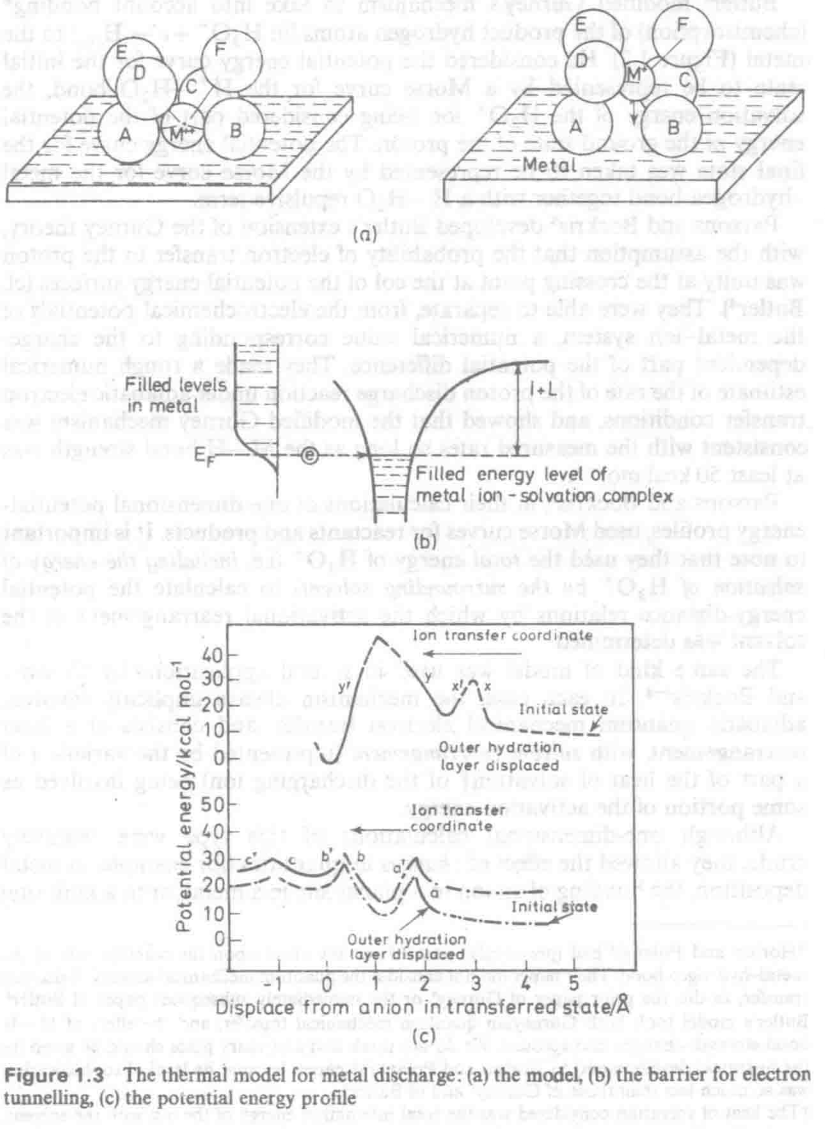

Figure 1.3 The thermal model for metal discharge: (a) the model, (b) the barrier for electron tunnelling, (c) the potential energy profile

to be roughly calculated. In this way, predictions were obtained concerning the likelihood of alternative paths for certain electrode reactions[9]. In particular, this model was applied to metal deposition[10], in which activation to the electron transfer condition was regarded as being due to thermal perturbation of the electrostatic ion–dipole interaction (cf. Figure 1.3).

At about the same time that these calculations were being published, Gerischer[11–13] applied the Gurney[1] thermal activation model to redox reactions in a detailed way. He extended the considerations to the electron distribution within the substrate, and developed the quantum theory of electron transfer between semi-conductors and ions in solution.

These developments of Gurney's model had not taken into account one important factor, namely, the quantum mechanical properties of the discharging proton itself. However, in a treatment not connected to the development of general electrode kinetic theory, the quantum properties of protons at interfaces had been considered at an early stage, by Bawn and Ogden[14], who calculated the rate of transition of a proton and a deuterium ion across an Eckart barrier (c.f. Bernal and Fowler[81], Conway, Bockris and Linton[80], who considered quantum mechanical effects in homogeneous systems). Later, Christov[15–18] developed a particularly detailed picture of the quantum mechanical transfer of protons, in several mechanistic interpretations of data on separation factors. Conway[19] showed that given certain assumptions concerning barrier width, proton tunnelling in the hydrogen discharge reaction could affect markedly the Tafel slope and give a potential-dependence of separation factor.

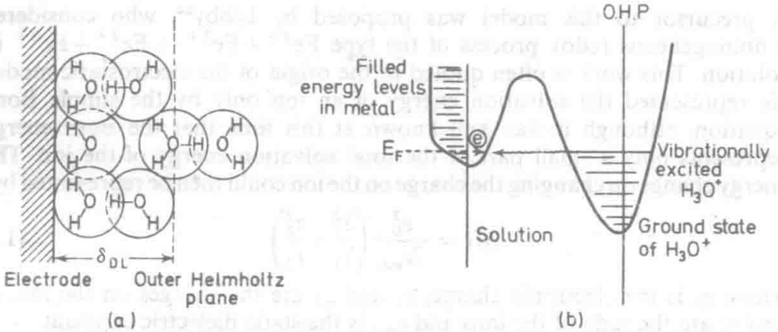

Figure 1.4 The Bockris and Matthews proton tunnelling model: (a) the model, (b) the barrier for proton tunnelling (Eckart barrier)

Some detailed calculations of the quantum mechanics of electrode reactions involving protons were carried out by Bockris and Matthews[20]. They calculated the effect of quantum mechanical penetration of protons through the classical transfer barrier from the H_3O^+ ion (interacting with the surrounding water molecules) to the electrode. Neutralisation was assumed to take place upon penetration of the barrier (Figure 1.4).

The Bockris and Matthews model was therefore fully quantum mechanical