Wiley Series on Electrocatalysis and
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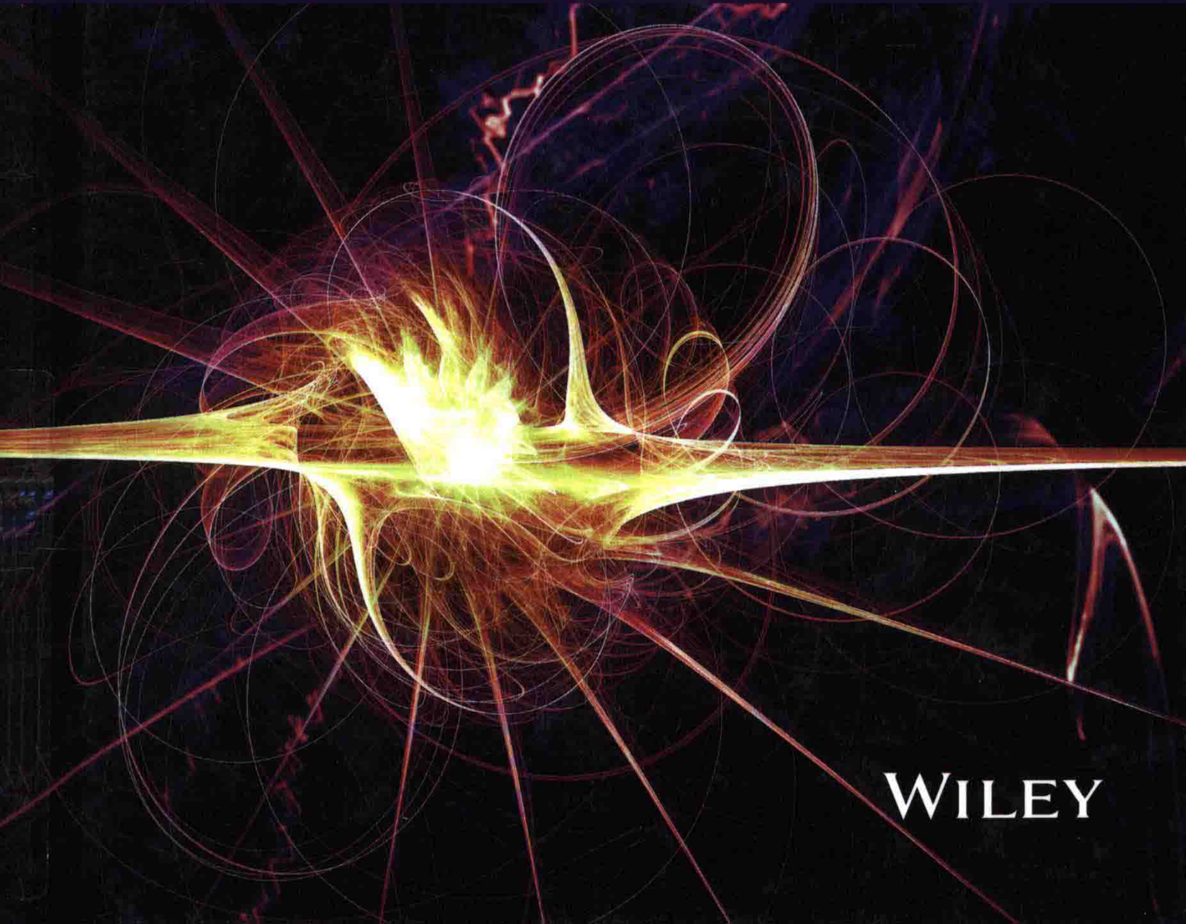
ELECTROCHEMICAL PROCESSES IN BIOLOGICAL SYSTEMS

Edited by Andrzej Lewenstam and Lo Gorton



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PREFACE

This series covers recent advancements in electrocatalysis and electrochemistry and depicts prospects for their contribution into the present and future of the industrial world. It aims to illustrate the transition of electrochemical sciences from its beginnings as a solid chapter of physical chemistry (covering mainly electron transfer reactions, concepts of electrode potentials, and structure of electrical double layer), to the field in which electrochemical reactivity is shown as a unique chapter of heterogeneous catalysis; is supported by high-level theory; connects to other areas of science; and includes focus on electrode surface structure, reaction environment, and interfacial spectroscopy.

The scope of this series ranges from electrocatalysis (practice, theory, relevance to fuel cell science, and technology), to electrochemical charge transfer reactions, biocatalysis, and photoelectrochemistry. While individual volumes may appear quite diverse, the series promises updated and overall synergistic reports providing insights to help further our understanding of the properties of electrified solid/liquid systems. Readers of the series will also find strong reference to theoretical approaches for predicting electrocatalytic reactivity by such high-level theories as density functional theory. Beyond the theoretical perspective, further vehicles for growth are such significant topics such as energy storage, syntheses of catalytic materials via rational design, nanometer-scale technologies, prospects in electrosynthesis, new instrumentation, and surface modifications. In this context, the reader will notice that new methods being developed for one field may be readily adapted for application in another.

Electrochemistry and electrocatalysis have both benefited from numerous monographs and review articles due to their depth, complexity, and relevance to the practical world. The Wiley Series on Electrocatalysis and Electrochemistry is dedicated to present the current activity by focusing each volume on a specific topic that is timely and promising in terms of its potential toward useful science and technology. The chapters in these volumes will also demonstrate the connection of electrochemistry to other disciplines beyond chemistry and chemical engineering, such as physics, quantum mechanics, surface science, and biology. The integral goal is to offer a broad-based analysis of the total development of the fields. The progress of the series will provide a global definition of what electrocatalysis and electrochemistry are now, and will contain projections about how these fields will further evolve in time. The purpose is twofold—to provide a modern reference for graduate instruction and for active researchers in the two disciplines, as well as to document that electrocatalysis and electrochemistry are dynamic fields that are expanding rapidly, and are likewise rapidly changing in their scientific profiles and potential.

Creation of each volume required the editor's involvement, vision, enthusiasm, and time. The Series Editor thanks each Volume Editor who graciously accepted his invitation. Special thanks go to Ms. Anita Lekhwani, the Series Acquisitions Editor, who extended the invitation to edit this series to me and has been a wonderful help in its assembling process.

ANDRZEJ WIECKOWSKI
Series Editor

CONTENTS

1

MODELING OF RELATIONS BETWEEN IONIC FLUXES AND MEMBRANE POTENTIAL IN ARTIFICIAL MEMBRANES

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1.1 INTRODUCTORY CONSIDERATIONS

A membrane can be regarded as a phase, finite in space, which separates two other phases and exhibits individual resistances to the permeation of different species (Schlögl's definition cited in [1]). The membranes can be of different thickness, from thin used typically for biological and artificial bilayers (in the range of a few nanometers) to relatively thick (hundreds of micrometers) used typically in ion-selective electrodes. A particular case is a membrane separating two electrolyte solutions, where ions are transferable species. In such a case, different modes of ion transport are possible: (i) Brownian motion; (ii) diffusion, resulting from concentration gradient; and (iii) migration as transport under the influence of an electrical field.

A general prerequisite related to the presence of charged species is electroneutrality condition of the membrane. However, even if electroneutrality is held on a macroscopic scale, charge separation effects appear, mainly at membrane/solution interfaces, resulting in the formation of potential difference. Taking into account possible chemical and electrical forces present in the system, assuming for simplicity one-dimensional

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transfer along the x-axis only, the flux of ion "i," J_i, across the membrane can be described as

$$J_i = -kU_i c_i \frac{\partial \bar{\mu}_i}{\partial x} \tag{1.1}$$

where k is a constant; U_i, c_i, and $\bar{\mu}_i$ are electrical mobility, concentration, and electrochemical potential of ion "i," respectively; and x is the distance from the membrane/solution interface. Using a well-known definition of electrochemical potential and assuming that the activity of ion "i" is equal to the concentration, this equation can be transformed to

$$J_i = -kU_i c_i \left(\frac{RT \partial \ln c_i}{\partial x} + z_i F \frac{\partial \varphi}{\partial x} \right) \tag{1.2}$$

with φ as the Galvani potential of the phase.

Since mobility, U_i, is a ratio of the transfer rate, v, and potential gradient $(\partial\varphi/\partial x)$, while the flux under influence of the electrical force is $J = vc$, it follows from Equation (1.2) that $k = 1/|z_i|F$. Taking then into account the Einstein relation, concerning diffusion coefficient, $D_i = U_i RT/|z_i|F$, Equation (1.2) can be rewritten as

$$J_i = -D_i \left(\frac{\partial c_i(x,t)}{\partial x} + \frac{z_i F}{RT} c_i(x,t) \frac{\partial \varphi(x,t)}{\partial x} \right) \tag{1.3}$$

This is the Nernst–Planck equation, relating the flux of ionic species, "i," to gradients of potential and concentration, being generally functions of distance, x, and time, t.

The Nernst–Planck equation is a general expression describing transport phenomena in membranes. Unfortunately, as differential equations deal with functions dependent on distance and time, solving of this equation is neither easy nor straightforward. However, under some conditions, simplifications of this equation are possible.

(i) For the equilibrium case, summary fluxes of all ionic species are zero, $J_i = 0$. In such a case,

$$\frac{\partial \ln c_i}{\partial x} = -\frac{z_i F}{RT} \frac{\partial \varphi}{\partial x} \tag{1.4}$$

After rearrangement and integration across the whole membrane (of thickness d), the well-known form is obtained:

$$\varphi_R - \varphi_L = \Delta\varphi_{\text{mem}} = \frac{RT}{z_i F} \ln \frac{c_R}{c_L} \tag{1.5}$$

where R and L refer arbitrarily to "right" and "left" hand side (membrane/solution interface) and c_R and c_L are solution concentrations at "right" and "left" interfaces.

This equation describing a membrane potential, $\Delta\varphi_{\text{mem}}$, is equivalent of the typical Nernst equation.

(ii) For the case of a neutral substance, $z_i = 0$, or in the absence of electrical driving force $(\partial\varphi/\partial x) = 0$, the Nernst–Planck equation reduces to Fick's equation, describing diffusional transport:

$$J_i = -D_i\left(\frac{\partial c_i}{\partial x}\right) \tag{1.6}$$

Solutions of the Nernst–Planck equation can be more easily obtained for the steady state, when the ionic fluxes $J_i = \text{const}$ and a time-independent version of the equation can be used. In this case, the Nernst–Planck equation can be applied to calculate potential difference in the membrane for given values of concentrations and mobilities. However, this procedure also requires integration, which can be difficult in some cases. Therefore, additional approximations are often used [2, 3]. The most known and used solutions are the Goldman and Henderson approximations.

1.1.1 Goldman Approximation and Goldman–Hodgkin–Katz Equation

This approximation assumes linearity of potential gradient across the membrane (i.e., constant electrical field in the membrane). This approximation is usually applicable to thin biological membranes, where charge prevails only in the surface areas of the membrane. In such a case, the derivative $(\partial\varphi/\partial x)$ can be approximated by the term $(\varphi_R - \varphi_L)/d$ leading to the simplified Nernst–Planck equation:

$$J_i = -\left(D_i\frac{\partial c_i}{\partial x} + \frac{z_i F}{RT}c_i\frac{\varphi_R - \varphi_L}{d}\right) \tag{1.7}$$

Under constant field condition, a steady state is practically obtained ($J_i = \text{const}$) and the Goldman flux equation can be derived:

$$J_i = \frac{z_i F D_i(\varphi_R - \varphi_L)}{dRT}\cdot\frac{c_i(\text{R}) - c_i(\text{L})\exp(-(z_i F(\varphi_R - \varphi_L))/RT)}{\exp(-(z_i F(\varphi_R - \varphi_L))/RT) - 1} \tag{1.8}$$

In the absence of transmembrane potential, $\varphi_R - \varphi_L \sim 0$, this equation simplifies to the well-known diffusion equation in a steady state.

Taking into account that the sum of individual ionic contributions to electrical current is zero (denoting the absence of applied external current),

$$\sum_{i=1}^{n} z_i J_i = 0 \tag{1.9}$$

further rearrangements are possible. For a simplified case of solution of ions of ±1 charge (e.g., Na^+, K^+, Cl^-), the equation describing the potential difference across the membrane (under steady-state conditions) can be obtained:

$$\varphi_R - \varphi_L = \frac{RT}{F}\ln\frac{D_{Na^+}c_{Na^+}(L) + D_{K^+}c_{K^+}(L) + D_{Cl^-}c_{Cl^-}(R)}{D_{Na^+}c_{Na^+}(R) + D_{K^+}c_{K^+}(R) + D_{Cl^-}c_{Cl^-}(L)} \tag{1.10}$$

It can be also assumed that ions take part in ion-exchange equilibrium, between the membrane and bathing electrolyte solution (sol) from the right or left hand side, (Eq. 1.11a) and (Eq. 1.11b), respectively:

$$c_i(R) = k_i c_i(\text{sol}, R) \tag{1.11a}$$

$$c_i(L) = k_i c_i(\text{sol}, L) \tag{1.11b}$$

with partition coefficients k_i of the species "i" between the solution and membrane phases. Then, introducing the permeability coefficient, P_i, $P_i = U_i k_i/|z_i|Fd$, Equations (1.10) and (1.11) can be transformed to the Goldman–Hodgkin–Katz equation, expressing the membrane potential as a function of ion concentrations in bathing solutions on both sides of the membrane and partition (permeability) coefficients:

$$\varphi_R - \varphi_L = \frac{RT}{F}\ln\frac{P_{Na^+}c_{Na^+}(L) + P_{K^+}c_{K^+}(L) + P_{Cl^-}c_{Cl^-}(R)}{P_{Na^+}c_{Na^+}(R) + P_{K^+}c_{K^+}(R) + P_{Cl^-}c_{Cl^-}(L)} \tag{1.12}$$

This equation is applicable, for example, to describe resting potentials of biological membranes.

1.1.2 Henderson Approximation

This approximation assumes linear concentration gradient across the membrane, while the electrical field need not be constant [4]. This approximation is usually applied to describe diffusion (liquid junction) potentials, particularly for the case of ion-selective electrodes. This potential can be approximated by the equation

$$\Delta\varphi_{LJ} = -\frac{RT}{F}\cdot\frac{\sum z_i u_i (c_i(R) - c_i(L))}{\sum z_i^2 u_i (c_i(R) - c_i(L))}\ln\frac{\sum z_i^2 u_i c_i(R)}{\sum z_i^2 u_i c_i(L)} \tag{1.13}$$

where u_i is $U_i/|z_i|F$.

Membrane processes related to charge separation and transport of charged species concern both biological membranes in cell biology (or artificial membranes having significant importance in separation processes) and membranes used in electroanalytical chemistry, for example, in ion-selective electrodes. However, in contrast to similarity of physicochemical phenomena occurring in all membranes containing mobile charged species, the description related to biological or separation membranes is different from that applicable to membranes of ion-selective electrodes. Therefore, the considerations in the following were divided into two sections: (i) related to more general description typical for separation and biological membranes where typically the Nernst–Planck equation is applicable and (ii) related to membranes used in ion-selective electrodes. In case (ii), practical and historical conditions result in dominance of simple empirical equations for the membrane potentials; however, in the last decade, the role of a more general theory using the Nernst–Planck equation is increasing.

1.2 GENERAL CONSIDERATIONS CONCERNING MEMBRANE POTENTIALS AND TRANSFER OF IONIC SPECIES

1.2.1 Boundary and Diffusion Potentials

Separation membranes are important both in biology and various technological areas: fuel cells, dialysis, reverse osmosis, separation of mixtures components, etc. These membranes can be generally described as neutral or charged membranes. For the former class of membranes, size exclusion and specific chemical interactions are the main factors responsible for selective permeability, while for charged membranes with incorporated ionic sites, electrostatic interactions are of substantial significance.

For the charged membranes, the membrane potential, understood as a potential difference between two electrolyte solutions (of different concentration or/and composition) separated by the membrane, is an important parameter characterizing their properties [5]. Measurements of membrane potential offer also a straightforward method for studying transport processes of charged species. Due to difficulties in solving the Nernst–Planck equation in a general case, simplifications are used, as they were shortly described in the previous section.

In the discussion given in the following, only cases with no external current flow are considered. In the description of membrane potentials, mostly a simplified formalism is used, expressed in terms of classical model proposed by Sollner [6], Teorell, Meyer, and Sievers [7, 8]. This model postulates splitting the potential prevailing in the system into three components: boundary potentials on the membrane (left and right side)/bathing solution interfaces and membrane bulk diffusion potential resulting from different mobility of ionic species as well as ion-exchange reactions leading to inhomogeneities in the interior of the membrane. It should be noted that the Teorell–Meyer–Sievers theory is applicable to fixed-site membranes with one kind of monovalent cations and anions as transferable species. It can be not valid for liquid membranes, where ionic sites are mobile.

Boundary potentials are regarded as equilibrium potentials resulting from ion exchange on the interface between the charged membrane and solution. In the case of equilibrium, assuming that activity coefficients are equal to 1, the change of chemical potential of transferable ion, "i," is equal to zero:

$$\Delta\mu_{\mathrm{i}} = 0 \tag{1.14}$$

The chemical standard potentials, $\mu^0_{\mathrm{i,m}}$ and $\mu^0_{\mathrm{i,s}}$, in the membrane and in the solution, respectively, can be different, determining the value of the distribution coefficient of species, "i" and k_i:

$$k_\mathrm{i} = \exp\left[\frac{-\left(\mu^0_{\mathrm{i,m}} - \mu^0_{\mathrm{i,s}}\right)}{RT}\right] \tag{1.15}$$

Then, assuming the existence of ion-exchanging sites in the membrane (unable to be released from the membrane), the boundary potential at a chosen membrane/solution interface can be represented by the Donnan potential, $\Delta\varphi_\mathrm{D} = \varphi^\mathrm{m} - \varphi^\mathrm{s}$ [9]:

$$RT \ln \frac{k_\mathrm{i} c^\mathrm{m}_\mathrm{i}}{c^\mathrm{s}_\mathrm{i}} + z_\mathrm{i} F \Delta\varphi_\mathrm{D} = 0 \tag{1.16}$$

where superscripts "m" and "s" relate to the membrane and solution phases, respectively.

The dependence of the Donnan potential on the electrolyte concentration in solution can be derived from Equation (1.16) taking into account electroneutrality condition in the membrane phase. In the case of a membrane with fixed ionic site concentration, X, and for 1:1 electrolyte (with cation M^+ and anion A^-) of concentration c, assuming the absence of specific interactions of ions with the membrane components ($k_\mathrm{i} = 1$), the Donnan potential is expressed by equation [10]

$$\Delta\varphi_\mathrm{D} = \varphi^\mathrm{m} - \varphi^\mathrm{s} = \pm \frac{RT}{F} \ln\left[\frac{X}{2c} + \left(1 + \left(\frac{X}{2c}\right)^2\right)^{\frac{1}{2}}\right] \tag{1.17}$$

with sign "+" or "−" for anion- or cation-exchanging membrane, respectively.

From this equation, two limiting cases follow (Fig. 1.1). For dilute solutions, when $c \ll X$, the concentration of counterions in the membrane is practically equal to X (with negligible concentrations of coions, this is the so-called Donnan exclusion case), and the Donnan potential becomes a linear function of $\ln c$ with positive or negative Nernstian slope, for cation and anion exchanger, respectively. On the other hand, for high electrolyte concentrations, when $c \gg X$, concentrations of counter- and coions in the membrane are almost equal; the Donnan potential is independent of electrolyte concentration and close to zero (Donnan exclusion failure).

In contrast to the equilibrium state observed at the membrane/solution interface, in the membrane interior, similar equilibria are typically not observed. In this case, different rates of ion transfer in the membrane result in diffusion potential formation, necessary to maintain a zero current steady state [1].

In order to calculate exact values of the diffusion potentials, knowledge about concentration profiles of all species in the membrane is needed. However, for practical purposes, some approximations can be used; the most popular is the Henderson