PHYSICAL
METHODS

OF CHEMISTRY

Second
Edition

Volume II

ELECTROCHEMICAL METHODS

Editors:
BRYANT W. ROSSITER
JOHN F. HAMILTON

PHYSICAL METHODS OF CHEMISTRY

Second Edition

Edited by

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Volume II

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Volume I	COMPONENTS OF SCIENTIFIC INSTRUMENTS AND APPLICATIONS OF COMPUTERS TO CHEMICAL RESEARCH
Volume II	ELECTROCHEMICAL METHODS

In Preparation:

Volume IIIA	DETERMINATION OF CHEMICAL COMPOSITION AND MOLECULAR STRUCTURE—PART A
Volume IIIB	DETERMINATION OF CHEMICAL COMPOSITION AND MOLECULAR STRUCTURE—PART B
Volume IVA	MICROSCOPY
Volume IVB	DIFFRACTION AND RESONANCE SPECTROSCOPICS
Volume V	DETERMINATION OF THERMODYNAMIC PROPERTIES
Volume VI	INVESTIGATIONS OF SURFACES AND INTERFACES
Volume VII	DETERMINATION OF ELECTRONIC AND OPTICAL PROPERTIES
Volume VIII	DETERMINATION OF ELASTIC AND MECHANICAL PROPERTIES

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PREFACE TO PHYSICAL METHODS OF CHEMISTRY

This is a continuation of a series of books started by Dr. Arnold Weissberger in 1945 entitled *Physical Methods of Organic Chemistry*. These books were part of a broader series, *Techniques of Organic Chemistry*, and were designated as Volume I of that series. In 1970, *Techniques of Chemistry* became the successor to and the continuation of the *Techniques of Organic Chemistry* series and its companion, *Techniques of Inorganic Chemistry*, reflecting the fact that many of the methods are employed in all branches of chemical sciences and the division into organic and inorganic chemistry had become increasingly artificial. Accordingly, the fourth edition of the series entitled *Physical Methods of Organic Chemistry* became *Physical Methods of Chemistry*, Volume I in the new *Techniques* series. That last edition of *Physical Methods of Chemistry* has had wide acceptance and it is found in most major technical libraries throughout the world. This new edition of *Physical Methods of Chemistry* will consist of eight or more volumes and is being published as a self-standing series to reflect its growing importance to chemists worldwide. This series will be designated as the second edition (the first edition, Weissberger and Rossiter, 1970) and will no longer be subsumed within *Techniques of Chemistry*.

This edition heralds profound changes in both the perception and practice of chemistry. The discernible distinctions between chemistry and other related disciplines have continued to shift and blur. Thus, for example, we see changes in response to the needs for chemical understanding in the life sciences. On the other hand, there are areas in which a decade or so ago only a handful of physicists struggled to gain a modicum of understanding but which now are standard tools of chemical research. The advice of many respected colleagues has been invaluable in adjusting the contents of the series to accomodate such changes.

Another significant change is attributable to the explosive rise of computers, integrated electronics, and other "smart" instrumentation. The result is the widespread commercial automation of many chemical methods previously learned with care and practiced laboriously. Faced with this situation, the task of a scientist writing about an experimental method is not straightforward.

Those contributing to *Physical Methods of Chemistry* were urged to adopt as their principal audience intelligent scientists, technically trained but perhaps inexperienced in the topic to be discussed. Such readers would like an introduction to the field together with sufficient information to give a clear understanding of the basic theory and apparatus involved and the appreciation for the value, potential, and limitations of the respective technique.

Frequently, this information is best conveyed by examples of application, and many appear in the series. Except for the purpose of illustration, however, no attempt is made to offer comprehensive results. Authors have been encouraged to provide ample bibliographies for those who need a more extensive catalog of *applications*, as well as for those whose goal is to become more expert in a *method*. This philosophy has also governed the balance of subjects treated with emphasis on the *method*, not on the results.

Given the space limitations of a series such as this, these guidelines have inevitably resulted in some variance of the detail with which the individual techniques are treated. Indeed, it should be so, depending upon the maturity of a technique, its possible variants, the degree to which it has been automated, the complexity of the interpretation, and other such considerations. The contributors, themselves expert in their fields, have exercised their judgment in this regard.

Certain basic principles and techniques have obvious commonality to many specialties. To avoid undue repetition, these have been collected in Volume I. We hope they will be useful on their own and will serve as reference material for other chapters.

We are deeply sorrowed by the death of our friend and associate, Dr. Arnold Weissberger, whose enduring support and rich inspiration had motivated this worthy endeavor through four decades and several editions of publication.

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March 1986

PREFACE

This volume begins with a general treatment of electrochemical theory common to all electroanalytical methods. Chapter 1, "Choosing and Performing an Electrochemical Experiment," is designed to assist those less familiar with the practice of electrochemistry in selecting particular electrodes or methods appropriate to a given need or problem. The more experienced electrochemist will find this chapter contains useful reference material, but will likely proceed directly to a method of choice. Chapter 7, "Spectroelectrochemistry," is new to the series and the technique involves a spectroscopic probe to monitor electrochemical events *in situ* with an intimate coupling of the electrochemical and spectrochemical process. This powerful new technique provides structural information about solution or absorbed species as well as redox information of the various chemical components. The remaining chapters contain the most recent information about the practice of various electrochemical techniques that over the years have proven to be of value in a wide variety of situations and applications.

We acknowledge our deep gratitude to the contributors who have spent long hours over manuscripts. We greet previous contributors, Dr. Eric R. Brown, Professor Louis Meites, Professor Royce W. Murray, and Dr. Michael Spiro, and welcome several new contributors to Volume II: Professor Zbigniew Galus, Professor William E. Geiger, Professor M. Dale Hawley, Professor Robert Kalvoda, Dr. Thomas R. Kissel, Professor Richard L. McCreery, Professor Lubomír Pospíšil, Dr. James R. Sandifer, Professor Antonín A. Vlček, and Professor Jiří Volke.

We are also extremely grateful to the many colleagues from whom we have sought counsel on the choice of subject matter and contributors. We express our gratitude to Mrs. Ann Nasella for her enthusiastic and skillful editorial assistance. In addition, we heartily thank the specialists whose critical readings of the manuscripts have frequently resulted in the improvements accrued from collective wisdom. For Volume II they are Dr. E. S. Brandt, Dr. E. R. Brown, Mrs. A. Kocher, Dr. J. R. Lenhard, Dr. G. L. McIntire, Dr. F. D. Saeva, and Dr. J. R. Sandifer.

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ELECTROCHEMICAL METHODS

CONTENTS

Chapter 1

CHOOSING AND PERFORMING AN ELECTROCHEMICAL EXPERIMENT

William E. Geiger and M. Dale Hawley

1 INTRODUCTION

Electrochemical techniques have been developed to a high degree and have helped address a myriad of problems involving redox chemistry. With the versatility and benefits of electrochemistry increasingly recognized over the past two decades, more nonspecialists have used this method on chemical problems. This chapter is intended to provide an aid to those who are not greatly experienced in electrochemical methods, but who seriously want to begin using these techniques effectively. The organization of the chapter derives from practical considerations, revolving around the questions most frequently facing a new investigator: Which technique should be used for a particular application? What solvent and supporting electrolyte should be used? What are the advantages of different metals as working electrodes? Which reference electrodes are most suitable? How should the electrochemical cell be designed? How are solution resistance problems best dealt with?

Although we have striven for a systematic approach, space limitations necessitate a fairly cursory look at these questions. Voltammetric techniques are discussed in detail in other chapters of this volume, and many of the practical experimental aspects have been reviewed more extensively elsewhere. In an effort organized around experimental rather than theoretical considerations, there is bound to be a substantial personal component to the treatment, based on the experiences and prejudices of the authors. It is hoped, however, that the nature and level of the treatment will provide a suitable introduction to those beginning electrochemical work.

1.1 Reversibility of Redox Couples

A typical electrochemical reaction is given in (1). In this model, the oxidized and reduced forms of the redox couple, Ox and Red, respectively, are interrelated by a transfer of n electrons,

$$\mathrm{Ox} + ne^- \xrightleftharpoons{k_s} \mathrm{Red} \xrightleftharpoons{k_c} \mathrm{Z} \qquad (1)$$

at the electrode surface. The primary electrode product, Red, may not be stable, and may undergo follow-up homogeneous chemical reactions in solution to give another product(s) Z. There may also be chemical reactions coupled to Ox, not shown in (1), which determine the availability of Ox to undergo the reduction. The rate constants of the heterogeneous reactions and homogeneous coupled reactions determine the reversibility of the redox couple. The standard heterogeneous electron-transfer rate constant, k_s or k^0, is the value of this quantity at the standard potential, E^0. In a perfectly reversible system, k_s is large enough that Ox and Red remain in equilibrium at the electrode surface, with the equilibrium value determined by the Nernst equation, (2):

$$E_{\text{app}} = E^0 - 2.3\frac{RT}{nF}\log\frac{a_{\text{Red}}}{a_{\text{Ox}}} \tag{2}$$

where 2.3 $RT/F = 0.059$ V at 298 K.

In practice, the observation of "Nernstian" behavior depends not only on the value of k_s but also on the time scale of the experiment that probes the concentrations of Ox and Red. Dc polarography is a much longer time-scale experiment than is, for example, ac polarography, since the time scale of the former is determined by drop time of the mercury electrode and of the latter by the inverse of the ac frequency. Consequently, even moderate charge-transfer kinetics can make a system appear Nernstian in dc polarography; such an *electrochemically reversible* system need have only a k_s greater than about 2×10^{-2} cm/s [1]. On the slow end of the charge-transfer phenomenon, systems with rate constants below about 3×10^{-5} cm/s are termed *electrochemically irreversible*, and rate constants between these limits yield *quasi-reversible* processes.

Quite distinct from the charge-transfer step are considerations of the stability of the primary electrolysis product, Red. If Red can be quantitatively reoxidized back to Ox, the couple is said to be *chemically* reversible. Again, this depends on the time scale of the experiment. An ac polarographic experiment might probe the stability of Red over the time frame of a millisecond, whereas bulk coulometry provides similar information over much longer periods, approximately 0.5 h. A system that is reversible in both the electrochemical and chemical sense is termed *totally* reversible.

1.2 Goals of the Experiment

Perhaps the earliest question to be asked by the experimentalist should concern the goals of the experiment, for they determine the techniques chosen. Some of the more common goals of electrochemical work are: qualitative or quantitative analysis of an inorganic ion or organic compound, at moderate to trace concentrations; determination of the n-value of a redox process and the reversibility (and E^0 value) of the couple; measurement of electron-transfer rates; mechanistic studies, especially probing the existence of radical ions or other transient intermediates; probing of the chemical and physical properties of electrogenerated compounds (coupling spectroscopy with electrochemistry, probing the reactions of electrogenerated species); synthesis of compounds by electrochemical methods.

Most electrochemical methods can yield at least some information about any or all of these questions. But each method, as well as each set of experimental conditions, is optimum for helping with one or another aspect of the problem.

2 ELECTROANALYTICAL TECHNIQUES

2.1 The General Problem

The fundamental quantities in electroanalytical chemistry are potential, current, concentration, and time. The relationship among these quantities will often be complex and dependent upon which of these parameters are being controlled, the mode of mass transfer, the kinetics of both the heterogeneous electron-transfer reaction and the homogeneous chemical reactions that accompany electron transfer, and the geometries of the working electrode and the cell. In this short overview of several of the more important electroanalytical techniques, numerous simplifying assumptions must be made. Unless it is stated otherwise, it will be assumed that: (1) the rate of electron transfer between the electroactive species and the electrode surface is rapid; (2) neither the oxidized nor the reduced form of the redox couple is involved in any solution reaction; (3) neither form of the redox couple is adsorbed on the electrode surface; (4) the working electrode is planar; and (5) the thickness of the solution layer immediately adjacent to the working electrode surface is small with respect to the perpendicular distance between the planar electrode surface and the cell wall. This last restriction rules out the important class of electrochemical methods involving thin-layer electrodes.

The three-electrode configuration is standard in the modern potentiostats and galvanostats that are used for the control of potential and current, respectively. The electrodes consist of the (1) working electrode at which the redox process of interest occurs, (2) the auxiliary electrode, which is the second current-carrying electrode in the cell, and (3) the reference electrode, which carries no cell current and to which the potential of the working electrode is referred. Unless coulometric electrolyses are being performed, it is usually unnecessary to isolate the working and auxiliary electrodes.

The electrochemical response is also dependent upon the mode of transport. To minimize the electrolysis times in coulometric electrolyses, fresh solution is continually brought to the large working electrode by forced convection. This may involve stirring the solution, either by mechanical means or by an inert gas; rotation or vibration of the working electrode; or a combination of solution stirring and movement of the electrode surface. The mode of mass transfer in the remaining electrochemical methods of interest to us is diffusion. Migration is specifically eliminated as an important mode of mass transfer by the addition of a large excess of inert supporting electrolyte, for example, Et_4NClO_4.

The reversible, one-electron reduction of species A to its stable anion radical, $A^{\overline{\cdot}}$ (3), causes A to be depleted in the layer of solution that is immediately adjacent to the electrode surface.

$$A + e^- \rightleftharpoons A^{\overline{\cdot}} \tag{3}$$

The electrolytic reduction of A creates a concentration gradient that causes A to diffuse from the bulk of solution to the electrode surface. If diffusion is the only mode of mass transfer by which A is transported to the electrode surface, then the partial differential equation that describes the concentration of A as a function of both time t and distance x from the electrode is

$$\frac{\partial C_A(x,t)}{\partial t} = D_A \frac{\partial^2 C_A(x,t)}{\partial x^2} \tag{4}$$

where D_A is the diffusion coefficient for species A and has the units of cm^2/s [2]. To solve this partial differential equation, appropriate boundary and initial conditions that are unique for each electrochemical technique must be specified. If the solution is initially homogeneous with respect to species A, then the initial condition for all methods is simply $C_A(x, t=0) = C_A^b$, where C_A^b is the bulk concentration of species A. In addition, because thin-layer techniques are excluded by restriction number 5 above; that is, the thickness of the solution layer immediately adjacent to the working electrode surface is small with respect to the perpendicular distance between the planar electrode surface and the cell wall, the boundary condition for all t as x approaches infinity will be $C_A(x=\infty, t) = C_A^b$. This leaves only the boundary condition at $x=0$ to be specified for each electroanalytical method.

2.2 Chronoamperometry

In the chronoamperometric method, the potential is stepped from a value where no faradaic process occurs to a potential sufficiently negative that the concentration of species A at the electrode surface will be effectively zero (Figure 1.1a). Since this makes the applicable boundary condition at the electrode surface $C_A(x=0, t>0) = 0$, (4) can now be solved by appropriate methods to give the concentration of species A for all values of x and t (5) [1]:

$$C_A(x, t) = C_A^b \operatorname{erf}(\lambda) \tag{5}$$

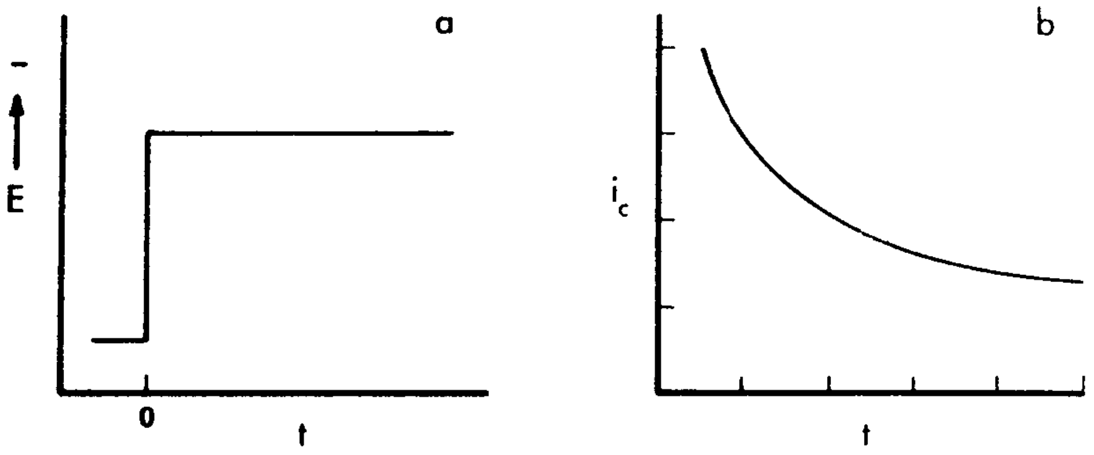

Figure 1.1 (a) The forcing function for chronoamperometry: At time $t=0$, the potential of the working electrode is stepped from a value where no faradaic process occurs to a value sufficiently negative that the concentration of species A at the electrode surface is rendered zero. (b) The response function: If the reduction of A to A^- is diffusion controlled, the current i is predicted by the Cottrell equation (7) to be inversely proportional to $t^{1/2}$. In aprotic solvent systems and with unshielded planar electrodes, reasonable agreement of experimental data with the model can often be obtained for t in the range $10^{-3}\ s \leqslant t \leqslant 10\ s$.

where $\lambda = x/2(D_A t)^{1/2}$ and $\mathrm{erf}(\lambda)$ is the error integral defined as

$$\mathrm{erf}(\lambda) = \frac{2}{\pi^{1/2}} \int_0^{\lambda} e^{-z^2}\, dz \qquad (6)$$

Equation (5) has been plotted for $D = 10^{-5}$ cm^2/s and for values of t equal to 10^{-1} s, 1 s, and 10 s (Figure 1.2). It should be noted from these two curves that the concentration gradient, $\partial C_A(x,t)/\partial x$, decreases with increasing t for all values of x. In addition, the thickness of the solution layer in which the concentration of species A is affected significantly by the electrode surface is given approximately by $2(D_A t)^{1/2}$ [when the argument of the error function in (5) is 1, that is, $x = 2(D_A t)^{1/2}$, the value of the error function is 0.85].

The instantaneous current that will be observed in this experiment is given by the expression

$$i = nFAD_A \left.\frac{\partial C_A(x,t)}{\partial x}\right|_{x=0} \qquad (7)$$

where A is the electrode area, n is the number of electrons, and the other terms have their usual significance. Differentiation of (5) with respect to x, subsequent evaluation of the derivative at $x = 0$, and substitution into (7) affords the Cottrell equation (8):

$$i = \frac{nFAD_A^{1/2} C_A^b}{(\pi t)^{1/2}} \qquad (8)$$

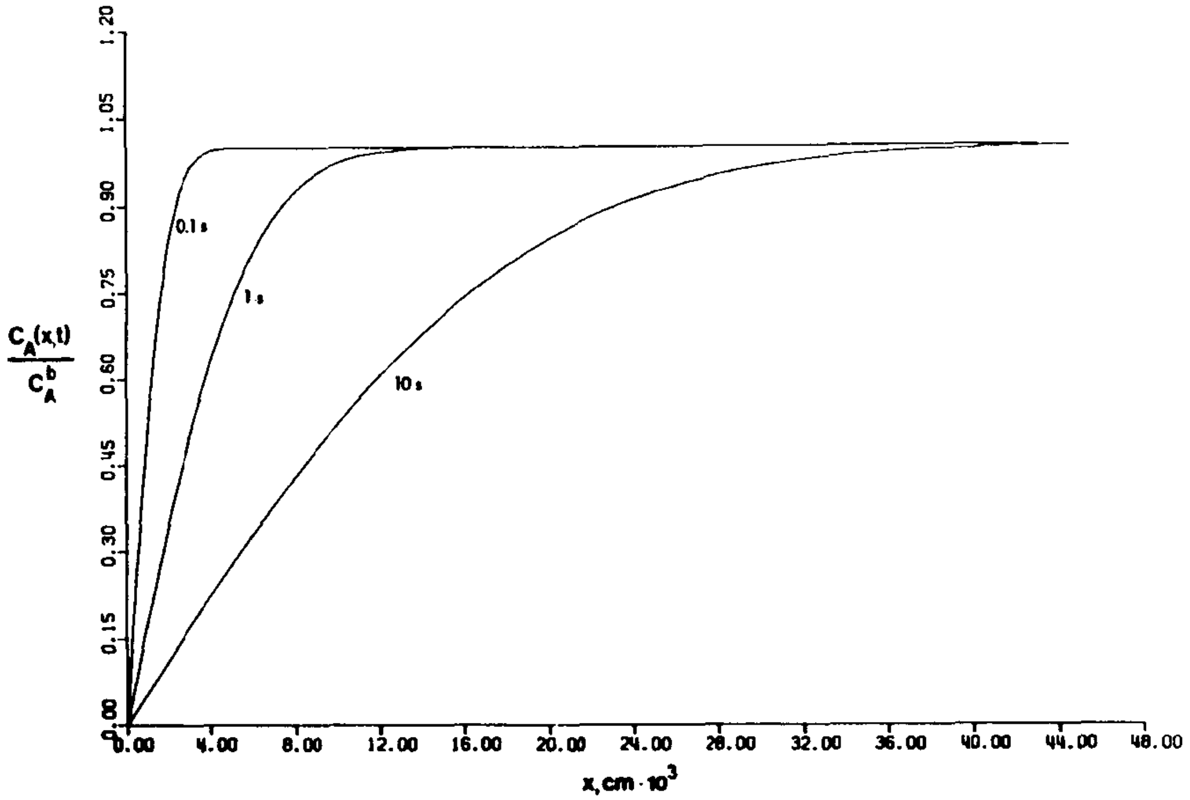

Figure 1.2 Plot of $C_A(x,t)/C_A^b$ versus distance x from a planar electrode surface for $t = 10^{-1}$ s and 1 s for the diffusion-controlled, chronoamperometric reduction of A.