# Electrochemical Systems

# Third Edition

John Newman Karen E. Thomas-Alyea



## ELECTROCHEMICAL SYSTEMS

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Third Edition

JOHN NEWMAN and KAREN E. THOMAS-ALYEA

University of California, Berkeley



ELECTROCHEMICAL SOCIETY SERIES



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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.

Published simultaneously in Canada.

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#### Library of Congress Cataloging-in-Publication Data:

Newman, John S., 1938–
Electrochemical systems / John Newman and Karen E. Thomas-Alyea.— 3rd ed. p. cm.
Includes bibliographical references and index.
ISBN 0-471-47756-7 (cloth)
I. Electrochemistry, Industrial. I. Thomas-Alyea, Karen E. II. Title.
TP255.N48 2004
660'.297-dc22

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## PREFACE TO THE THIRD EDITION

This third edition incorporates various improvements developed over the years in teaching electrochemical engineering to both graduate and advanced undergraduate students. Chapter 1 has been entirely rewritten to include more explanations of basic concepts. Chapters 2, 7, 8, 13, 18, and 22 and Appendix C have been modified, to varying degrees, to improve clarity. Illustrative examples taken from real engineering problems have been added to Chapters 8 (kinetics of the hydrogen electrode), 18 (cathodic protection), and 22 (reaction-zone model and flow-through porous electrodes). Some concepts have been added to Chapters 2 (Pourbaix diagrams and the temperature dependence of the standard cell potential) and 13 (expanded treatment of the thermoelectric cell). The exponential growth of computational power over the past decade, which was made possible in part by advances in electrochemical technologies such as semiconductor processing and copper interconnects, has made numerical simulation of coupled nonlinear problems a routine tool of the electrochemical engineer. In realization of the importance of numerical simulation methods, their discussion in Appendix C has been expanded.

As discussed in the preface to the first edition, the science of electrochemistry is both fascinating and challenging because of the interaction among thermodynamic, kinetic, and transport effects. It is nearly impossible to discuss one concept without referring to its interaction with other concepts. We advise the reader to keep this in mind while reading the book, in order to develop facility with the basic principles as well as a more thorough understanding of the interactions and subtleties.

#### XVI PREFACE TO THE THIRD EDITION

We have much gratitude for the many graduate students and colleagues who have worked on the examples cited and proofread chapters and for our families for their continual support. KET thanks JN for the honor of working with him on this third edition.

> JOHN NEWMAN Berkeley, California

KAREN E. THOMAS-ALYEA Manchester, Connecticut

## PREFACE TO THE SECOND EDITION

A major theme of *Electrochemical Systems* is the simultaneous treatment of many complex, interacting phenomena. The wide acceptance and overall impact of the first edition have been gratifying, and most of its features have been retained in the second edition. New chapters have been added on porous electrodes and semiconductor electrodes. In addition, over 70 new problems are based on actual course examinations.

Immediately after the introduction in Chapter 1, some may prefer to study Chapter 11 on transport in dilute solutions and Chapter 12 on concentrated solutions before entering the complexities of Chapter 2. Chapter 6 provides a less intense, less rigorous approach to the potentials of cells at open circuit. Though the subjects found in Chapters 5, 9, 10, 13, 14, and 15 may not be covered formally in a onesemester course, they provide breadth and a basis for future reference.

The concept of the electric potential is central to the understanding of the electrochemical systems. To aid in comprehension of the difference between the potential of a reference electrode immersed in the solution of interest and the electrostatic potential, the quasi-electrostatic potential, or the cavity potential—since the composition dependence is quite different—Problem 6.12 and Figure 12.1 have been added to the new edition. The reader will also benefit by the understanding of the potential as it is used in semi-conductor electrodes.

## PREFACE TO THE FIRST EDITION

Electrochemistry is involved to a significant extent in the present-day industrial economy. Examples are found in primary and secondary batteries and fuel cells; in the production of chlorine, caustic soda, aluminum, and other chemicals; in electroplating, electromachining, and electrorefining; and in corrosion. In addition, electrolytic solutions are encountered in desalting water and in biology. The decreasing relative cost of electric power has stimulated a growing role for electrochemistry. The electrochemical industry in the United States amounts to 1.6 percent of all U.S. manufacturing and is about one third as large as the industrial chemicals industry.<sup>1</sup>

The goal of this book is to treat the behavior of electrochemical systems from a practical point of view. The approach is therefore macroscopic rather than microscopic or molecular. An encyclopedic treatment of many specific systems is, however, not attempted. Instead, the emphasis is placed on fundamentals, so as to provide a basis for the design of new systems or processes as they become economically important.

Thermodynamics, electrode kinetics, and transport phenomena are the three fundamental areas which underlie the treatment, and the attempt is made to illuminate these in the first three parts of the book. These areas are interrelated to a considerable extent, and consequently the choice of the proper sequence of material is a problem. In this circumstance, we have pursued each subject in turn, notwithstanding the necessity of calling upon material which is developed in detail only at a later point. For example, the open-circuit potentials of electrochemical

<sup>1</sup>G. M. Wenglowski, "An Economic Study of the Electrochemical Industry in the United States," J. O'M. Bockris, ed., *Modern Aspects of Electrochemistry*, no. 4 (London: Butterworths, 1966), pp. 251-306.

cells belong, logically and historically, with equilibrium thermodynamics, but a complete discussion requires the consideration of the effect of irreversible diffusion processes.

The fascination of electrochemical systems comes in great measure from the complex phenomena which can occur and the diverse disciplines which find application. Consequences of this complexity are the continual rediscovery of old ideas, the persistence of misconceptions among the uninitiated, and the development of involved programs to answer unanswerable or poorly conceived questions. We have tried, then, to follow a straightforward course. Although this tends to be unimaginative, it does provide a basis for effective instruction.

The treatment of these fundamental aspects is followed by a fourth part, on applications, in which thermodynamics, electrode kinetics, and transport phenomena may all enter into the determination of the behavior of electrochemical systems. These four main parts are preceded by an introductory chapter in which are discussed, mostly in a qualitative fashion, some of the pertinent factors which will come into play later in the book. These concepts are illustrated with rotating cylinders, a system which is moderately simple from the point of view of the distribution of current.

The book is directed toward seniors and graduate students in science and engineering and toward practitioners engaged in the development of electrochemical systems. A background in calculus and classical physical chemistry is assumed.

William H. Smyrl, currently of the University of Minnesota, prepared the first draft of Chapter 2, and Wa-She Wong, formerly at the General Motors Science Center, prepared the first draft of Chapter 5. The author acknowledges with gratitude the support of his research endeavors by the United States Atomic Energy Commission, through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory, and subsequently by the United States Department of Energy, through the Materials Sciences Division of the Lawrence Berkeley Laboratory.

## INTRODUCTION

Electrochemical techniques are used for the production of aluminum and chlorine, the conversion of energy in batteries and fuel cells, sensors, electroplating, and the protection of metal structures against corrosion, to name just a few prominent applications. While applications such as fuel cells and electroplating may seem quite disparate, in this book we show that a few basic principles form the foundation for the design of all electrochemical processes.

The first practical electrochemical system was the Volta pile, invented by Alexander Volta in 1800. Volta's pile is still used today in batteries for a variety of industrial, medical, and military applications. Volta found that when he made a sandwich of a layer of zinc metal, paper soaked in salt water, and tarnished silver and then connected a wire from the zinc to the silver, he could obtain electricity (see Figure 1.1). What is happening when the wire is connected? Electrons have a chemical preference to be in the silver rather than the zinc, and this chemical preference is manifest as a voltage difference that drives the current. At each electrode, an electrochemical reaction is occurring: zinc reacts with hydroxide ions in solution to form free electrons, zinc oxide, and water, while silver oxide (tarnished silver) reacts with water and electrons to form silver and hydroxide ions. Hydroxide ions travel through the salt solution (the electrolyte) from the silver to the zinc, while electrons travel through the external wire from the zinc to the silver.

We see from this example that many phenomena interact in electrochemical systems. Driving forces for reaction are determined by the thermodynamic properties of the electrodes and electrolyte. The rate of the reaction at the interface in

*Electrochemical Systems, Third Edition*, by John Newman and Karen E. Thomas-Alyea ISBN 0-471-47756-7 (© 2004 John Wiley & Sons, Inc.



Figure 1.1 Volta's first battery, comprised of a sandwich of zinc with its oxide layer, salt solution, and silver with its oxide layer. While the original Volta pile used an electrolyte of NaCl in water, modern batteries use aqueous KOH to increase the conductivity and the concentration of  $OH^-$ .

response to this driving force depends on kinetic rate parameters. Finally, mass must be transported through the electrolyte to bring reactants to the interface, and electrons must travel through the electrodes. The total resistance is therefore a combination of the effects of reaction kinetics and mass and electron transfer. Each of these phenomena—thermodynamics, kinetics, and transport—is addressed separately in subsequent chapters. In this chapter, we define basic terminology and give an overview of the principal concepts that will be derived in subsequent chapters.

#### 1.1 DEFINITIONS

Every electrochemical system must contain two electrodes separated by an electrolyte and connected via an external electronic conductor. Ions flow through the electrolyte from one electrode to the other, and the circuit is completed by electrons flowing through the external conductor.

An *electrode* is a material in which electrons are the mobile species and therefore can be used to sense (or control) the potential of electrons. It may be a metal or other electronic conductor such as carbon, an alloy or intermetallic compound, one of many transition-metal chalcogenides, or a semiconductor. In particular, in electrochemistry an electrode is considered to be an electronic conductor that carries out an electrochemical reaction or some similar interaction with an adjacent phase. Electronic conductivity generally decreases slightly with increasing temperature and is of the order  $10^2$  to  $10^4$  S/cm, where a siemen (S) is an inverse ohm.

An *electrolyte* is a material in which the mobile species are ions and free movement of electrons is blocked. Ionic conductors include molten salts, dissociated salts in solution, and some ionic solids. In an ionic conductor, neutral salts are found to be dissociated into their component ions. We use the term *species* to refer to ions as well as neutral molecular components that do not dissociate. Ionic conductivity

generally increases with increasing temperature and is of the order  $10^{-4}$  to  $10^{-1}$  S/cm, although it can be substantially lower.

In addition to these two classes of materials, some materials are *mixed conductors*, in which charge can be transported by both electrons and ions. Mixed conductors are occasionally used in electrodes, for example, in solid-oxide fuel cells.

Thus the key feature of an electrochemical cell is that it contains two electrodes that allow transport of electrons, separated by an electrolyte that allows movement of ions but blocks movement of electrons. To get from one electrode to the other, electrons must travel through an external conducting circuit, doing work or requiring work in the process.

The primary distinction between an electrochemical reaction and a chemical redox reaction is that, in an electrochemical reaction, reduction occurs at one electrode and oxidation occurs at the other, while in a chemical reaction, both reduction and oxidation occur in the same place. This distinction has several implications. In an electrochemical reaction, oxidation is spatially separated from reduction. Thus, the complete redox reaction is broken into two *half-cells*. The rate of these reactions can be controlled by externally applying a potential difference between the electrodes, for example, with an external power supply, a feature absent from the design of chemical reactors. Finally, electrochemical reactions are always heterogeneous; that is, they always occur at the interface between the electrolyte and an electrode (and possibly a third phase such as a gaseous or insulating reactant).

Even though the half-cell reactions occur at different electrodes, the rates of reaction are coupled by the principles of conservation of charge and *electroneutrality*. As we demonstrate in Section 3.1, a very large force is required to bring about a spatial separation of charge. Therefore, the flow of current is continuous: All of the current that leaves one electrode must enter the other. At the interface between the electrode and the electrolyte, the flow of current is still continuous, but the identity of the charge-carrying species changes from being an electron to being an ion. This change is brought about by a charge-transfer (i.e., electrochemical) reaction. In the electrolyte, electroneutrality requires that there be the same number of equivalents of cations as anions:

$$\sum_{i} z_i c_i = 0, \tag{1.1}$$

where the sum is over all species *i* in solution, and  $c_i$  and  $z_i$  are the concentration and the charge number of species *i*, respectively. For example,  $z_{Zn^{2+}}$  is +2,  $z_{OH^-}$  is -1, and  $z_{H_2O}$  is 0.

*Faraday's law* relates the rate of reaction to the current. It states that the rate of production of a species is proportional to the current, and the total mass produced is proportional to the amount of charge passed multiplied by the equivalent weight of the species:

$$m_i = -\frac{s_i M_i l t}{n F},\tag{1.2}$$

#### 4 INTRODUCTION

where  $m_i$  is the mass of species *i* produced by a reaction in which its *stoichiometric* coefficient is  $s_i$  and *n* electrons are transferred,  $M_i$  is the molar mass, *F* is Faraday's constant, equal to 96,487 coulombs/equivalent, and the total amount of charge passed is equal to the current *I* multiplied by time *t*. The sign of the stoichiometric coefficient is determined by the convention of writing an electrochemical reaction in the form

$$\sum_{i} s_{i} M_{i}^{z_{i}} \rightleftharpoons n e^{-}, \qquad (1.3)$$

where here  $M_i$  is the symbol for the chemical formula of species *i*. For example, for the reaction

$$\operatorname{Zn} + 2\operatorname{OH}^{-} \rightleftharpoons \operatorname{ZnO} + 2e^{-} + H_2O,$$
 (1.4)

 $s_{ZnO}$  is -1,  $s_{OH^-}$  is 2, and *n* is 2.

Following historical convention, current is defined as the flow of positive charge. Thus, electrons move in the direction opposite to that of the convention for current flow. *Current density* is the flux of charge, that is, the rate of flow of positive charge per unit area perpendicular to the direction of flow. The behavior of electrochemical systems is determined more by the current density than by the total current, which is the product of the current density and the cross-sectional area. In this text, the symbol i refers to current density unless otherwise specified.

Owing to the historical development of the field of electrochemistry, several terms are in common use. *Polarization* refers to the departure of the potential from equilibrium conditions caused by the passage of current. *Overpotential* refers to the magnitude of this potential drop caused by resistance to the passage of current. Below, we will discuss different types of resistances that cause overpotential.

#### **1.2 THERMODYNAMICS AND POTENTIAL**

If one places a piece of tarnished silver in a basin of salt water and connects the silver to a piece of zinc, the silver spontaneously will become shiny, and the zinc will dissolve. Why? An electrochemical reaction is occurring in which silver oxide is reduced to silver metal while zinc metal is oxidized. It is the thermodynamic properties of silver, silver oxide, zinc, and zinc oxide that determine that silver oxide is reduced spontaneously at the expense of zinc (as opposed to reducing zinc oxide at the expense of the silver). These thermodynamic properties are the *electrochemical potentials*. Let us arbitrarily call one half-cell the right electrode and the other the left electrode. The energy change for the reaction is given by the change in Gibbs free energy for each half-cell reaction:

$$\Delta G = \left(\sum_{i} s_{i} \mu_{i}\right)_{\text{right}} - \left(\sum_{i} s_{i} \mu_{i}\right)_{\text{left}},\tag{1.5}$$

where G is the Gibbs free energy,  $\mu_i$  is the electrochemical potential of species *i*, and  $s_i$  is the stoichiometric coefficient of species *i*, as defined by equation 1.3. If  $\Delta G$  for the reaction with our arbitrary choice of right and left electrodes is negative, then the electrons will want to flow spontaneously from the left electrode to the right electrode. The right electrode is then the more positive electrode, which is the electrode in which the electrons have a lower electrochemical potential. This is equivalent to saying that  $\Delta G$  is equal to the free energy of the products minus the free energy of the reactants.

Now imagine that instead of connecting the silver directly to the zinc, we connect them via a high-impedance potentiostat, and we adjust the potential across the potentiostat until no current is flowing between the silver and the zinc. (A *potentiostat* is a device that can apply a potential, while a *galvanostat* is a device that can control the applied current. If the potentiostat has a high internal impedance (resistance), then it draws little current in measuring the potential.) The potential at which no current flows is called the *equilibrium* or *open-circuit* potential, denoted by the symbol U. This equilibrium potential is related to the Gibbs free energy by

$$\Delta G = -nFU. \tag{1.6}$$

The equilibrium potential is thus a function of the intrinsic nature of the species present, as well as their concentrations and, to a lesser extent, temperature.

While no net current is flowing at equilibrium, random thermal collisions among reactant and product species still cause reaction to occur, sometimes in the forward direction and sometimes in the backward direction. At equilibrium, the rate of the forward reaction is equal to the rate of the backward reaction. The potential of the electrode at equilibrium is a measure of the electrochemical potential (i.e., energy) of electrons in equilibrium with the reactant and product species. Electrochemical potential will be defined in more detail in Chapter 2. In brief, the electrochemical potential can be related to the molality  $m_i$  and activity coefficient  $\gamma_i$  by

$$\mu_i = \mu_i^{\theta} + RT \ln m_i \gamma_i, \qquad (1.7)$$

where  $\mu^{\theta}$  is independent of concentration, R is the universal gas constant (8.3143 J/mol·K), and T is temperature in kelvin. If one assumes that all activity coefficients are equal to 1, then equation 1.5 reduces to the Nernst equation

$$U = U^{\theta} - \frac{RT}{nF} \ln\left(\prod_{i} m_{i}^{s_{i}}\right)_{\text{right}} + \frac{RT}{nF} \ln\left(\prod_{i} m_{i}^{s_{i}}\right)_{\text{left}},$$
 (1.8)

which relates the equilibrium potential to the concentrations of reactants and products. In many texts, one sees equation 1.8 without the "left" term. It is then implied that one is measuring the potential of the right electrode with respect to some unspecified left electrode.

By connecting an electrode to an external power supply, one can electrically control the electrochemical potential of electrons in the electrode, thereby

#### 6 INTRODUCTION

perturbing the equilibrium and driving a reaction. Applying a negative potential to an electrode increases the energy of electrons. Increasing the electrons' energy above the lowest unoccupied molecular orbital of a species in the adjacent electrolyte will cause reduction of that species (see Figure 1.2). This reduction current (flow of electrons into the electrode and from there into the reactant) is also called a *cathodic* current, and the electrode at which it occurs is called the *cathode*. Conversely, applying a positive potential to an electrode decreases the energy of electrons, causing electrons to be transferred from the reactants to the electrode. The electrode where such an oxidation reaction is occurring is called the anode. Thus, applying a positive potential relative to the equilibrium potential of the electrode will drive the reaction in the anodic direction; that is, electrons will be removed from the reactants. Applying a negative potential relative to the equilibrium potential will drive the reaction in the cathodic direction. Anodic currents are defined as positive (flow of positive charges into the solution from the electrode) while cathodic currents are negative. Common examples of cathodic reactions include deposition of a metal from its salt and evolution of H<sub>2</sub> gas, while common anodic reactions include corrosion of a metal and evolution of O<sub>2</sub> or Cl<sub>2</sub>.

Note that one cannot control the potential of an electrode by itself. Potential must always be controlled relative to another electrode. Similarly, potentials can be measured only relative to some reference state. While it is common in the physics literature to use the potential of an electron in a vacuum as the reference state (see Chapter 3), electrochemists generally use a *reference electrode*, an electrode designed so that its potential is well-defined and reproducible. A potential is well-defined if both reactant and product species are present and the kinetics of the reaction is sufficiently fast that the species are present in their equilibrium concentrations. Since potential is measured with a high-impedance voltmeter, negligible current passes through a reference electrode. Chapter 5 discusses commonly used reference electrodes.

Electrochemical cells can be divided into two categories: galvanic cells, which spontaneously produce work, and electrolytic cells, which require an input of work



Figure 1.2 Schematic of the relative energy of the electron in reduction and oxidation reactions. During a reduction reaction, electrons are transferred from the electrode to the lowest unoccupied energy level of a reactant species. During oxidation, electrons are transferred from the highest occupied energy level of the reactant to the electrode.

to drive the reaction. Galvanic applications include discharge of batteries and fuel cells. Electrolytic applications include charging batteries, electroplating, electrowinning, and electrosynthesis. In a galvanic cell, connecting the positive and negative electrodes causes a driving force for charge transfer that decreases the potential of the positive electrode, driving its reaction in the cathodic direction, and increases the potential of the negative electrode, driving its reaction in the anodic direction. Conversely, in an electrolytic cell, a positive potential (positive with respect to the equilibrium potential of the positive electrode) is applied to the positive electrode to force the reaction in the anodic direction, while a negative potential is applied to the negative electrode to drive its reaction in the cathodic direction. Thus, the positive electrode is the anode in an electrolytic cell while it is the cathode in a galvanic cell, and the negative electrode is the cathode in an electrolytic cell and the anode in a galvanic cell.

#### **1.3 KINETICS AND RATES OF REACTION**

Imagine that we have a system with three electrodes: a zinc negative electrode, a silver positive electrode, and another zinc electrode, all immersed in a beaker of aqueous KOH (see Figure 1.1). We pass current between the negative and positive electrodes. For the moment, let us just focus on one electrode, such as the zinc negative electrode. Since it is our electrode of interest, we call it the *working electrode*, and the other electrode through which current passes is termed the *counterelectrode*. The second zinc electrode will be placed in solution and connected to the working electrode through a high-impedance voltmeter. This second zinc electrode is in equilibrium with the electrolyte since no current is passing through it. We can therefore use this electrode as a reference electrode to probe changes in the potential in the electrolyte relative to the working electrode.

As mentioned above, a driving force is required to force an electrochemical reaction to occur. Imagine that we place our reference electrode in the solution adjacent to the working electrode. Recall that our working and reference electrodes are of the same material composition. Since no current is flowing at the reference electrode, and a potential has been applied to the working electrode to force current to flow, the difference in potential between the two electrodes must be the driving force for reaction. This driving force is termed the *surface overpotential* and is given the symbol  $\eta_s$ . The rate of reaction often can be related to the surface overpotential by the *Butler-Volmer equation*, which has the form

$$i = i_0 \left[ \exp\left(\frac{\alpha_a F}{RT} \eta_s\right) - \exp\left(-\frac{\alpha_c F}{RT} \eta_s\right) \right].$$
(1.9)

A positive  $\eta_s$  produces a positive (anodic) current. The derivation and application of the Butler-Volmer equation, and its limitations, is discussed in Chapter 8. As mentioned above, random thermal collisions cause reactions to occur in both the

forward and backward directions. The first term in equation 1.9 is the rate of the anodic direction, while the second term is the rate of the cathodic direction. The difference between these rates gives the net rate of reaction. The parameter  $i_0$  is called the *exchange current density* and is analogous to the rate constant used in chemical kinetics. In a reaction with a high exchange current density, both the forward and backward reactions occur rapidly. The net direction of reaction depends on the sign of the surface overpotential. The exchange current density depends on the concentrations of reactants and products, temperature, and also the nature of the electrode–electrolyte interface and impurities that may contaminate the surface. Each of these factors can change the value of  $i_0$  by several orders of magnitude.  $i_0$  can range from over 1 mA/cm<sup>2</sup> to less than  $10^{-7}$  mA/cm<sup>2</sup>. The parameters  $\alpha_a$  and  $\alpha_c$ , called apparent transfer coefficients, are additional kinetic parameters that relate how an applied potential favors one direction of reaction over the other. They usually have values between 0.2 and 2.

A reaction with a large value of  $i_0$  is often called fast or reversible. For a large value of  $i_0$ , a large current density can be obtained with a small surface overpotential.

The relationship between current density and surface overpotential is graphed in Figures 1.3 and 1.4. In Figure 1.3, we see that the current density varies linearly with  $\eta_s$  for small values of  $\eta_s$ , and from the semilog graph given in Figure 1.4 we see that the current density varies exponentially with  $\eta_s$  for large values of  $\eta_s$ . The latter observation was made by Tafel in 1905, and Figure 1.4 is termed a *Tafel plot*. For large values of the surface overpotential, one of the terms in equation 1.9 is negligible, and the overall rate is given by either

$$i = i_0 \exp\left(\frac{\alpha_a F}{RT} \eta_s\right)$$
 (for  $\alpha_a F \eta_s \gg RT$ ) (1.10)

or

$$i = -i_0 \exp\left(-\frac{\alpha_c F}{RT}\eta_s\right)$$
 (for  $\alpha_c F \eta_s \ll -RT$ ). (1.11)

The *Tafel slope*, either  $2.303RT/\alpha_a F$  or  $2.303RT/\alpha_c F$ , thus depends on the apparent transfer coefficient.

#### 1.4 TRANSPORT

The previous section describes how applying a potential to an electrode creates a driving force for reaction. In addition, the imposition of a potential difference across an electronic conductor creates a driving force for the flow of electrons. The driving force is the *electric field* **E**, related to the gradient in potential  $\Phi$  by

$$\mathbf{E} = -\nabla\Phi. \tag{1.12}$$