# 1

# Overview of Electrode Processes



Electrochemistry allows the controlled addition or removal of electrons, often one by one, at molecules or ions arriving very near a metallic or semiconducting electrode. Electrochemical systems provide access to fundamental chemical events and valuable practical applications; however, the science also entails complexity. Key events often take place in a tiny fraction of the total volume, typically at or very near metallic surfaces, or perhaps only at rare active sites on surfaces. The reacting molecules or ions must be transported to the locales of reaction, and the processes of transport influence reaction rates. Once a reaction is initiated at an electrode, it can proceed through a mechanism involving almost any kind of chemical step–proton transfer, a change in ligation, elimination, rearrangement, or even subsequent electron transfer–either at the electrode or with other molecules or ions. Reactions at electrodes involve the orbital structures of ions and molecules and the band structures of metals, semiconductors, and insulators. They depend, too, on electrostatics and thermodynamics. Among the domains of chemistry, electrochemistry offers some of the greatest challenges to effective theory and experimental examination; yet, over two centuries of genuine science, a strong base of theory and experimental methodology has been assembled. This book presents the most essential aspects.

Electrochemistry connects electrical and chemical effects. Much of it deals with either chemical changes caused by passage of an electric current or the production of electrical energy by chemical reactions. Yet, the field extends broadly to encompass diverse phenomena (e.g., electrophoresis and corrosion), devices (such as electrochromic displays, electroanalytical sensors, and fuel cells), and technologies (including portable power for electronic devices or automobiles, large-scale energy storage for load management on the electric power grid, electroplating of metals, and large-scale production of materials, such as aluminum and chlorine). While the basic principles of electrochemistry discussed in this text apply to all such topics, the main emphasis here is on the *application of electrochemical methods to the study of chemical systems*.

Scientists make electrochemical measurements for a variety of reasons. They may want to understand the kinetics of a reaction at an electrode, perhaps to speed it up, to inhibit it, or to optimize product yield. They may want to generate an unstable intermediate, such as a radical ion, and study its rate of decay or its spectroscopic properties. They may seek to analyze a solution for trace species. They may be interested in obtaining thermodynamic data about a reaction. In these examples, electrochemical methods are employed as tools in the study of chemical systems, much in the manner of spectroscopic methods. Many electrochemical methods have been devised. Their application requires an understanding of the fundamental principles of reactions at electrodes and the electrical properties of electrode/solution interfaces.

This chapter sets a stage. It introduces the terms and concepts used to describe electrochemical systems. In the process, it covers interfaces and cells; potential and current; reference electrodes and the measurement of potential; concepts of electrochemical experimentation;

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the dynamics behind current–potential curves; the extraction of chemical information from electrochemical responses; faradaic and nonfaradaic processes; double-layer structure and charging currents. The tour of ideas is designed to help the reader to establish an elementary working knowledge of electrochemical concepts and systems.

If the larger goal is to learn how to employ electrochemical methods reliably, far more is needed. The journey just begins in Chapter 1. The ideas and treatments introduced here are developed much more fully and rigorously in later chapters.

## 1.1 Basic Ideas

### 1.1.1 Electrochemical Cells and Reactions

In electrochemical systems, one is concerned with the processes and factors affecting the transport of charge across interfaces between adjacent chemical phases, most commonly between an electronic conductor (an *electrode*) and an ionic conductor (an *electrolyte*). Throughout this book, we will focus on the electrode/electrolyte interface and the events that occur there when an electric potential is applied and current passes.

Charge is transported through an electrode by the movement of electrons (and sometimes by "holes" in semiconductor electrodes). In an electrolyte, charge is carried by the movement of ions.[1] At the interface between an electrode and an electrolyte, the passage of charge requires that these distinct conduction modes be linked through an *electrode reaction*, causing electrons to be consumed or produced at the electrode and ions to be produced or consumed in the electrolyte. Examples include:

a) Plating of copper from an aqueous solution,

$$Cu^{2+} + 2e \rightarrow Cu \tag{1.1.1}$$

b) Production of hydrogen gas from alkaline water at a platinum electrode,

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \tag{1.1.2}$$

c) Generation of the nitrobenzene radical anion in acetonitrile at a gold electrode,

$$PhNO_2 + e \rightarrow PhNO_2^{\bullet -} \tag{1.1.3}$$

d) De-intercalation of lithium ion from a lithium cobalt oxide electrode in a lithium-ion battery, leaving an excess electron on the electrode to be used in an external circuit,

$$LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe \tag{1.1.4}$$

e) Oxidation of stable ruthenium(II) complexes in water solution at a gold electrode,[2]

$$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e \tag{1.1.5}$$

Typical electrode materials include solid metals (e.g., Pt, Au), liquid metals (e.g., Hg, amalgams), carbon (e.g., graphite, graphene, glassy carbon), and semiconductors (indium–tin oxide, Si, GaAs, CdS). The most common electrolytes are liquid solutions containing ionic species,

1 Questions are sometimes asked about conduction in solutions by "free" electrons. Such species are very short lived and contribute negligibly to conductivity. "Solvated" electrons can exist in exceptional circumstances (Section 20.4), but are generally very reactive. Overwhelmingly, the mobile charges in solutions are ions, and electrons exchanged at an electrode are carried in solution by atoms, molecules, and ions.

2 bpy = 2,2′-bipyridine (Figure 1).

such as, $H^+$, $Na^+$, tetraalkylammonium, $Cl^-$, or $BF_4^-$ in water or a nonaqueous solvent. To be useful in an electrochemical cell, the solvent–electrolyte system must be of sufficiently low resistance (i.e., sufficiently conductive) for the electrochemical experiment envisioned. Less conventional electrolytes include fused salts (e.g., molten NaCl–KCl eutectic) and ionically conductive polymers (e.g., Nafion, polyethylene oxide–$LiClO_4$). Solid electrolytes also exist (e.g., sodium β-alumina, in which charge is carried by mobile sodium ions moving between aluminum oxide sheets).

It is natural to think about events at a single interface, but we will find that one cannot deal experimentally with an isolated boundary. Instead, one must study collections of interfaces called *electrochemical cells*, which are defined most generally as two electrodes separated by at least one electrolyte phase.

There is a shorthand notation for expressing the structures of cells. For example, that pictured in Figure 1.1.1*a* is written compactly as

$$\mathrm{Zn/Zn^{2+}, Cl^-/AgCl/Ag} \tag{1.1.6}$$

In this notation, a slash represents a phase boundary, and a comma separates two components in the same phase.[3] When a gaseous phase is involved, it is written adjacent to its corresponding conducting element. For example, the cell in Figure 1.1.1*b* is written schematically as

$$\mathrm{Pt/H_2/H^+, Cl^-/AgCl/Ag} \tag{1.1.7}$$

Generally, the electrodes in a cell are not at the same electrical potential. If the two electrodes are connected by a wire, electrons can move from the more negative electrode to the more positive, so that a chemical reaction can be sustained in the cell. Electrons produced on the negative electrode by an electrode reaction proceed to the positive electrode, where they feed a different electrode reaction, consuming the electrons. The overall chemical reaction taking place in a cell is made up of the independent *half-reactions* describing the separate chemical changes at the two electrodes. For example, the bidirectional half-reactions for the cell in (1.1.6) are $Zn^{2+} + 2e \rightleftharpoons Zn$ and $AgCl + e \rightleftharpoons Ag + Cl^-$. When the electrodes are connected, the reaction

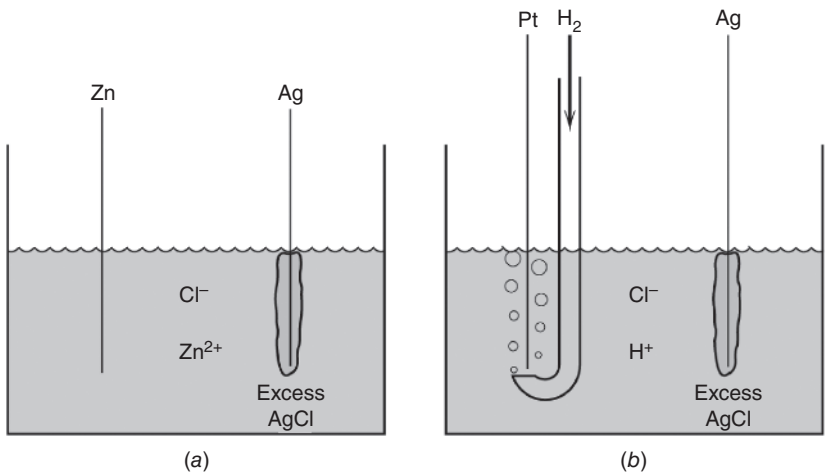


**Figure 1.1.1** Typical electrochemical cells. (*a*) Zn metal and Ag wire covered with AgCl immersed in an aqueous $ZnCl_2$ solution. (*b*) Pt wire in a stream of $H_2$ and Ag wire covered with AgCl in HCl solution.

3 A double slash, not yet used here, represents a phase boundary whose interfacial potential difference is regarded as a negligible component of the overall cell potential.

at zinc proceeds in the backward direction, while that at silver goes forward. Zinc dissolves and AgCl is converted to Ag + $Cl^-$. The net result is

$$Zn + 2AgCl \rightarrow Zn^{2+} + 2Ag + 2Cl^- \tag{1.1.8}$$

Processes 1.1.1–1.1.5 are all half-reactions. None can happen alone. Each must be coupled in a cell that includes a second interface with another half-reaction proceeding in the opposite direction.

### 1.1.2 Interfacial Potential Differences and Cell Potential

We will find in Chapter 2 that a transition in electric potential can generally be expected in crossing from one conducting phase to another. Moreover, it usually occurs in a narrow zone right at the interface. Thus, the electric potential changes in a stairstep fashion as one proceeds from one electrode, through the intervening conducting phases, to the other electrode. The situation is as depicted in Figure 1.1.2.

A high-impedance voltmeter enables one to measure a difference in electrical potential between the electrodes in a complete cell without perturbing the cell by drawing an appreciable current from it. This *cell potential* [in volts (V), where 1 V = 1 joule/coulomb (J/C)] expresses the energy available to drive charge externally between the electrodes and to do electrical work outside the cell. It is the sum of the individual interfacial potential differences encountered on the electrical path inside the cell from one electrode to another (shown as $E$ in Figure 1.1.2).

The potential difference between the electrodes is not merely to be *observed* in the manner just discussed. It can also be *deliberately altered* by connecting a power supply across the cell. As the applied voltage is adjusted, one can generally expect changes in the individual interfacial potential differences, especially at the electrode/electrolyte boundaries. Normally, the imposed voltage will differ from the open-circuit cell potential, and the cell will respond by drawing current from the power supply. By changing the imposed voltage, it is practical to drive the

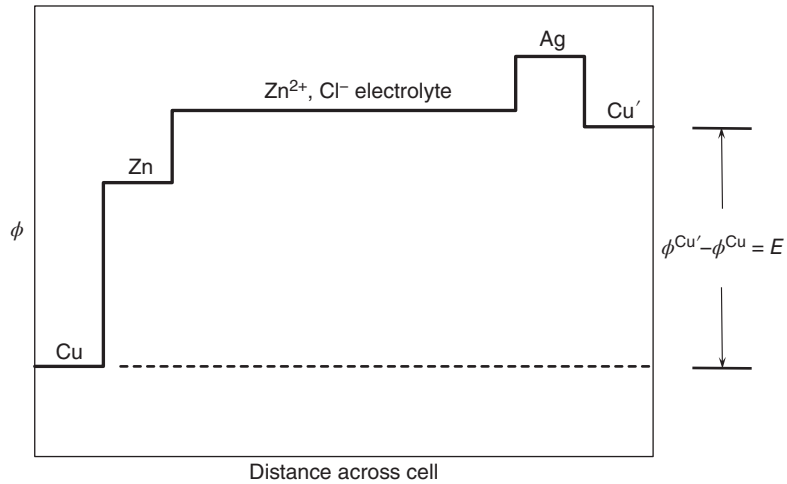


**Figure 1.1.2** Profile of electric potential, $\phi$, across Cu/Zn/$Zn^{2+}$, $Cl^-$/AgCl/Ag/Cu′ at equilibrium (open-circuit, zero current). The Cu and Cu′ represent contacts made to the cell in Figure 1.1.1*a* using copper wire. A cell potential can be measured only between two like phases. The AgCl is not in the electrical path because it is porous, and the electrolyte has direct access to the Ag. The AgCl is, however, a critical component of the half reaction, so it is included in the representation of the cell.

current in either direction. We will shortly be discussing the magnitude and chemical effects of the current.

A sharp transition in potential at a phase boundary implies that a high electric field exists there. One can expect it to influence the behavior of charge carriers (electrons or ions) in the interfacial region. More important, a potential difference at an interface affects the relative energies of electrons on opposite sides of the boundary; hence, it can determine the direction and the rate of electron transfer. Accordingly, the measurement and control of potential differences in a cell are among the most important aspects of experimental electrochemistry.

### 1.1.3 Reference Electrodes and Control of Potential at a Working Electrode

Even though it is always necessary to employ whole cells in electrochemical investigations, one's interest is usually in the behavior at only one of the electrodes, called the *working electrode*.[4] To focus on it, one can standardize the other half of the cell by using an electrode (called a *reference electrode*) that exhibits a reproducible, invariant potential difference at its electrode/electrolyte boundary. If one can build a cell in which a working electrode is paired with a well-behaved reference electrode, then any *change* in the cell potential must occur at the working electrode.

The key to such a reference electrode is to maintain a known, constant composition. If all participants in a half-reaction are present at an electrode/electrolyte interface [including both redox forms (e.g., both AgCl and Ag or both $H^+$ and $H_2$)], the interfacial potential difference turns out to be linked to the activities of those species near the electrode.[5] The *Nernst equation*, familiar from introductory chemistry, describes the behavior quantitatively (Section 2.1.6). By constructing a reference electrode of reproducible composition, one obtains a reproducible potential difference at the reference interface.

It is also important that the interfacial potential difference at the reference electrode not change when current passes through the cell and that the reference side of the cell not suffer contamination from the working side. We will soon see how these issues can be addressed. The design, construction, and use of reference electrodes make up a substantial topic of their own (Sections 2.1.8 and 2.5), but it should not divert us now. The present goal is just to introduce the concept of a reference electrode and to identify some common types.

The internationally accepted primary reference is the *standard hydrogen electrode* (SHE), or *normal hydrogen electrode* (NHE), which has all components at unit activity at 25 °C:[6]

$$\mathrm{Pt/H_2}(a = 1)/\mathrm{H^+}(a = 1,\ \text{aqueous}) \tag{1.1.9}$$

Since the NHE is not convenient from an experimental standpoint,[7] potentials are measured and quoted with respect to other reference electrodes. An important historic reference is the *saturated calomel electrode* (SCE), which is

$$\mathrm{Hg/Hg_2Cl_2/KCl\ (saturated\ in\ water)} \tag{1.1.10}$$

Its potential at 25 °C is 0.244 V *vs*. NHE.

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4 Sometimes called the *indicator electrode*.

5 *Activity* is a concept used extensively in thermodynamics to take account of the effects of concentrations, partial pressures, or mole fractions. See Section 2.1.5 for detail. For now, just think of it as a representation of concentration, pressure, or mole fraction, in which "unit activity" would correspond roughly to a 1 M solution, to a partial pressure of $10^5$ Pa (1 bar), or to a pure solid.

6 Thus, the NHE would involve something like 1 M $H^+$ and gaseous $H_2$ at close to 1 bar ($1.01325 \times 10^5$ Pa).

7 The NHE is not actually realizable except by extrapolation of the behavior of real electrodes. For now, it is not necessary for us to go into how this is done. We just need to recognize that the NHE is not an everyday reference electrode.

A more common reference, is the *silver/silver chloride electrode*,

Ag/AgCl/KCl (saturated in water) (1.1.11)

with a potential at 25 °C of 0.197 V *vs.* NHE. It is common to see potentials identified in the literature as "*vs.* Ag/AgCl" when this electrode is used.

When a cell potential is simply observed using a high-impedance voltmeter, no significant current is allowed to pass in the external circuit between the electrodes. In that situation, the working electrode potential would change only if the composition at the working electrode were to be altered, perhaps because of a pH change or because new species were added to the surrounding solution.

As mentioned above, it is also possible to shift the potential of the working electrode *vs.* the reference by connecting a power supply to these two electrodes, causing the cell potential to adopt the power supply's output voltage. Ideally, any change in the cell potential from that observed without connection to the power supply would show up at the working electrode, because the reference electrode is built to maintain a constant interfacial potential difference.[8] In this way, we might achieve the ability to control the working electrode's potential arbitrarily. In sections below, we will revisit that topic in detail.

### 1.1.4 Potential as an Expression of Electron Energy

We say in electrochemistry that we observe or control the *potential* of the working electrode *with respect to* the reference, which is equivalent to observing or controlling the energy of the transferable electrons on the working electrode, relative to electronic states in the electrolyte (1, 2) (Section 2.2.5). By driving the working electrode to more negative potentials, the energies of its electrons are raised. Very significant changes in energy can be achieved, because the potential can often be shifted over a range of several volts. For each volt, the energy of each electron on the working electrode changes by one electron–volt (1 eV),[9] which is 96.5 kJ per mole of electrons. This is a sizable change in energy—comparable to the activation energies or overall energy changes involved in many chemical reactions—comparable, as well, to the spacings between orbitals involved in chemical bonding.

The electrons on the electrode can reach a level high enough to transfer into vacant electronic states on species in the electrolyte. In that case, a flow of electrons from electrode to solution (a *reduction current*) occurs (Figure 1.1.3*a*). Similarly, the energy of the electrons can be lowered by imposing a more positive potential, and at some point, electrons on molecules or ions in the electrolyte will find a more favorable energy on the electrode and can transfer there. Their flow, from solution to electrode, is an *oxidation current* (Figure 1.1.3*b*). The critical potentials at which these processes occur are often related to the *standard potentials*, $E^0$, for the specific half-reactions in the system. We will have much more to say about standard potentials, especially in Chapter 2.

### 1.1.5 Current as an Expression of Reaction Rate

When the potential of the working electrode *vs.* the reference is varied by means of an external power supply, a current can flow in the external circuit, because electrons cross the

8 And because other interfacial potential differences in the system, such as those at metal–metal contacts (Figure 1.1.2) also remain constant.

9 The eV is a convenient unit of energy in electrochemical studies. It is the work required to move a positive test charge equal in magnitude to the electronic charge, *e*, across a barrier of 1 V. In general, $\Delta\mathbf{E} = q\Delta\phi$, where $\Delta\mathbf{E}$ is the change in energy, $q$ is the charge being moved, and $\Delta\phi$ is the electric potential difference across which the charge is moved. When $q$ is expressed in units of $e$ and $\Delta\phi$ is in V, $\Delta\mathbf{E}$ is in eV.

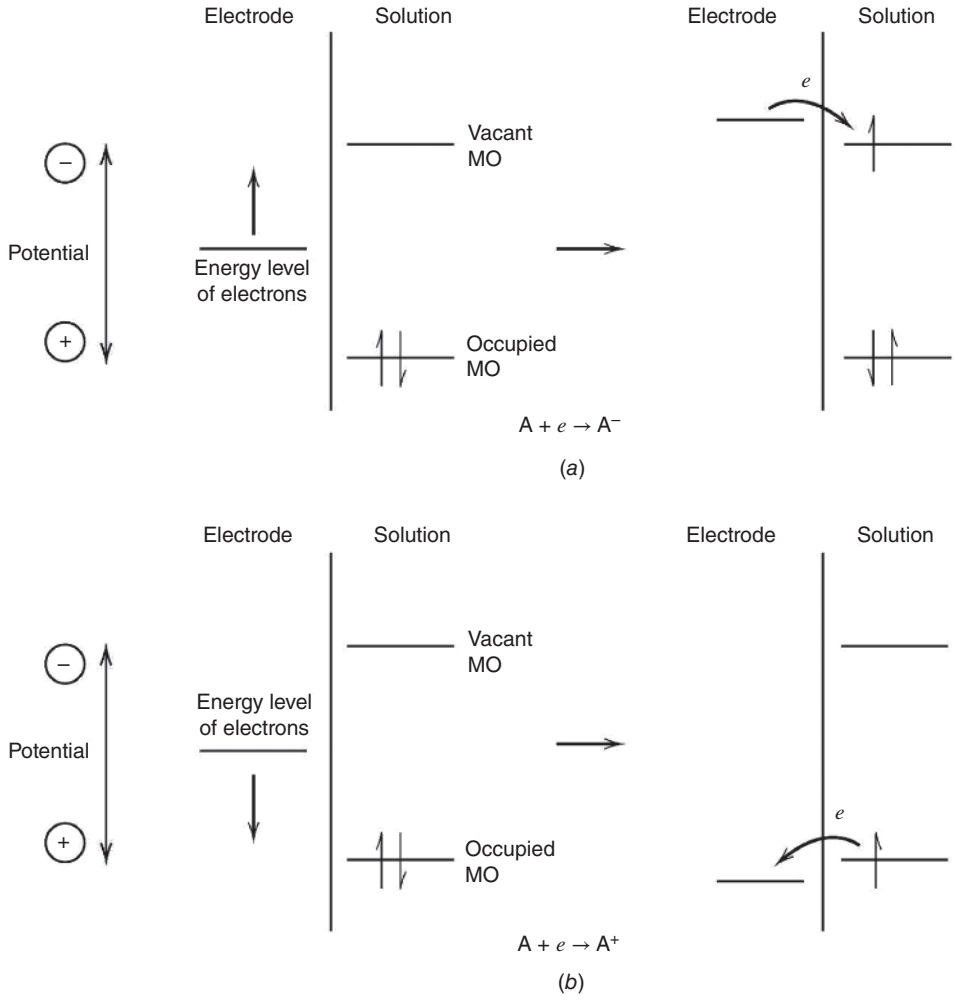



**Figure 1.1.3** Representation of (*a*) reduction and (*b*) oxidation of a species, A, in solution. The molecular orbitals (MO) shown for species A are the highest occupied MO and the lowest vacant MO. For simple one-electron reactions, these correspond in an approximate way to the $E^0$ values of the $A/A^-$ and $A^+/A$ couples, respectively. The illustrated system could represent an aromatic hydrocarbon like 9,10-diphenylanthracene in an aprotic solvent like acetonitrile at a platinum electrode.

electrode/solution interfaces as reactions occur. The number of electrons is related stoichiometrically to the amounts of reactant consumed and product generated. If an electrode reaction consumes or produces $n$ electrons for each reactant (e.g., $2e$ for the oxidation of Zn), then $n$ moles of electrons must flow in the external circuit for every mole of electroreactant transformed. The total charge, $Q$, on those electrons is

$$Q\,(\text{coulombs}) = nF\,(\text{coulombs/mol electrolyzed}) \times N\,(\text{mol electrolyzed}) \qquad (1.1.12)$$

where $F$ (the *Faraday constant*) is the charge on a mole of electrons, 96,485.3 C/mol. Equation (1.1.12) is known as *Faraday's law*. The passage of 96,485.3 C causes consumption of 1 mole of reactant and production of 1 mole of product in a simple one-electron reaction.[10]

10 The number of moles of electrons passed is sometimes called the number of *equivalents*.

The current, expressed in amperes (A), is the rate at which the total charge is collected,

$$i(\text{amperes}) = \frac{dQ}{dt}(\text{coulombs/s}) = nF\frac{dN}{dt} \tag{1.1.13}$$

$$\boxed{\text{Rate (mol/s)} = \frac{dN}{dt} = \frac{i}{nF}} \tag{1.1.14}$$

Thus, the current is a direct measure of the rate of the reaction at the working electrode.

Interpreting the rate of an electrode reaction is often more complex than for reactions occurring in solution or in the gas phase. The latter are called *homogeneous reactions* because they occur everywhere within the medium at a uniform rate. In contrast, electrode processes are *heterogeneous reactions*, occurring only at the electrode/electrolyte interface. Their rates depend on mass transfer to the electrode and various surface effects, in addition to the usual kinetic variables. Reaction rates, $\upsilon$, for heterogeneous reactions are usually given in units of mol/s per unit area of electrode surface, $A$; i.e.,

$$\boxed{\text{Rate}(\text{mol s}^{-1}\text{cm}^{-2}) = \upsilon = \frac{i}{nFA} = \frac{j}{nF}} \tag{1.1.15}$$

where $j$ is the *current density* (A/cm$^2$).

### 1.1.6 Magnitudes in Electrochemical Systems

It is common to characterize the scale of an electrochemical system according to the size of the working electrode, the magnitude of the current, the duration over which a current can be delivered, the timescale of an experimental perturbation, or the mass of reactant consumed or product created. Systems can be huge or tiny by any of these measures. Working electrodes can be as large as several square meters or as small as a square nanometer ($10^{-18}$ m$^2$). Current may be in the hundreds of thousands of amperes or in the picoamperes. A current might be required to last for nanoseconds or for years, and the timescales of experimental perturbations can extend from the indefinite to nanoseconds. The use of a system may involve no consumption of material, only a few atoms, or massive amounts. In the upper range, for example, the industrial production of metallic aluminum is wholly accomplished in electrochemical cells. The global economy produces about 50 million metric tons annually. The US share of this production (but less than 5% of the global total) still requires several percent of all US electric power production.

While this book is general in its presentation of electrochemical fundamentals, the real focus is on the experimental methodology used to measure properties of chemical systems or to investigate chemical behavior. We will be thinking about "lab-sized" cells convenient to bench-top work. They generally will not be larger than a few hundred mL, but they can be much, much smaller. Cells containing microliters are common. Indeed, cells have been made with volumes in the attoliter ($10^{-18}$ L) range.

In most experiments, we will seek only to probe the system, not to change its overall composition appreciably. A small working electrode is usually employed. It might be a disk (made by sealing a wire in glass and polishing a cross-section), an exposed length of wire, or a droplet. It might be as large as a few centimeters in diameter or length, but usually it is smaller, and the surface area is less than 0.1 cm$^2$. Much work has been done with very much smaller electrodes, e.g., with disks having diameters in the range of a few μm or even down to about 10 nm.

The equipment used to control and to observe electrochemical cells can sometimes deliver 1–10 A, but mostly it has less capacity. "Large" currents in lab-sized cells are 10–1000 mA. Currents at tiny working electrodes can be picoamperes ($10^{-12}$ A), or even smaller.

In the pictures we have drawn so far, the geometry of the electrodes has not been critical, and they might have been made roughly, perhaps of exposed wire or foil, without much regard for the surface area. As we become more sophisticated in our discussion, we will find that geometry is often very important in electrochemical systems. We will have to pay close attention to the shapes and sizes of electrodes and to their relative placement in the system.

### 1.1.7 Current–Potential Curves

A plot of the current at the working electrode *vs.* the potential of that electrode—a *current–potential (i – E) curve*—can be quite informative about reactions occurring at the working interface. Much of this book deals with how one obtains and interprets $i - E$ curves.

Let us consider the cell in Figure 1.1.4 and discuss in a qualitative way the current–potential curve that might be obtained from it. In Section 1.3 and in later chapters, we will be more quantitative. The first step is to consider the voltage measured by the high-impedance voltmeter when the switch is left open, so that no current passes through the cell. This voltage is called the *open-circuit potential* of the cell.[11]

#### *(a) Open-Circuit Potential*

For some electrochemical cells, like those in Figure 1.1.1, it is possible to calculate the open-circuit potential from thermodynamic data, i.e., via the Nernst equation from the

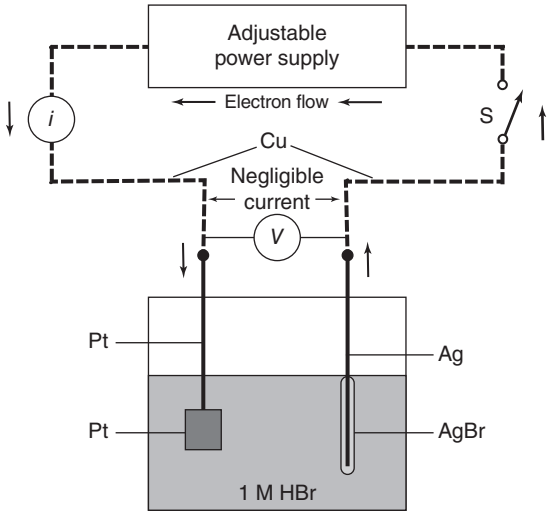



**Figure 1.1.4** Electrochemical cell Pt/$H^+$(1 M), $Br^-$(1 M)/AgBr/Ag attached to apparatus for obtaining a current–potential curve. The power supply is continuously tunable from positive to negative voltage. Switch, S, allows it to be connected or disconnected from the cell. In the depicted situation, the power supply is set to draw electrons, when the switch is closed, from the Ag/AgBr electrode (where Ag is converted to AgBr) and send them to the Pt electrode (where $H^+$ is converted to $H_2$). Arrows show the path of electron flow, which passes through ammeter, *i*, measuring the current. The high-impedance voltmeter, *V*, measures the potential difference between the two electrodes, but requires only a tiny current. External wiring is of Cu (dashed segments), so there are junctions between the Cu and the electrode materials, signified by the dots just below the voltmeter. Atmospheric $O_2$ has been removed from the cell, because it represents an interference to the processes of interest. Since the electroreduction of $O_2$ commonly interferes, most electrochemical cells are purged of $O_2$ by bubbling with nitrogen or other means.

11 Also called the *zero-current potential* or the *rest potential*. The term *rest potential* has been blurred in recent years by inconsistent usage. In this book, we will use only *open-circuit potential* or *zero-current potential* to avoid confusion.

standard potentials of the half-reactions involved at both electrodes (Section 2.1.6). The key requirement is that true equilibria must be established on both sides of the cell, because each electrode engages a pair of redox forms linked by a given half-reaction (i.e., a *redox couple*). In Figure 1.1.1*b*, for example, we have $H^+$ and $H_2$ at one electrode and Ag and AgCl at the other.[12]

The cell in Figure 1.1.4 is different, because an overall equilibrium cannot be established. At the Ag/AgBr electrode, a couple is present, and the half-reaction is

$$AgBr + e \rightleftharpoons Ag + Br^- \quad E^0 = 0.0711\ V\ vs.\ NHE \tag{1.1.16}$$

Since both AgBr and Ag are pure solids, their activities are unity. The activity of $Br^-$ can be found from the concentration in solution; hence, the potential of this electrode (with respect to NHE) can be calculated from the Nernst equation. This electrode is at equilibrium. However, we cannot calculate a thermodynamic potential for the Pt/$H^+$, $Br^-$ electrode, because we cannot identify a pair of redox forms coupled by a given half-reaction. The controlling pair clearly is not the $H^+/H_2$ couple, since no $H_2$ has been introduced into the cell. Consequently, the Pt electrode, and the cell as a whole, are not at equilibrium. An equilibrium cell potential does not exist.

Even though the equilibrium potential of the cell is not available from thermodynamic data, the cell does have a potential at open circuit, and we can place it within a range, as shown below. The actual value of the open-circuit potential in this case turns out to be governed by kinetics, as discussed in Chapter 3.

***(b) Background i–E Curve***

Let us now consider what happens when an adjustable power supply (even a battery bridged by a potentiometer) and a microammeter are connected across the cell by closing the switch shown in Figure 1.1.4, and the potential of the Pt electrode is gradually made more negative with respect to the Ag/AgBr electrode. The latter is a reference electrode because it is at equilibrium and has a fixed potential; thus, changes in the cell potential are manifested at the Pt electrode, which we can regard as the working electrode.[13]

The first electrode reaction that occurs at the Pt is the reduction of protons,

$$2H^+ + 2e \rightarrow H_2 \tag{1.1.17}$$

The direction of electron flow is from the electrode to protons in solution, as in Figure 1.1.3*a*, so a reduction (*cathodic*) current flows.

This result is shown graphically on the right side of Figure 1.1.5, our first example of a current–potential curve. In the convention used in this book, cathodic currents are taken as positive, and negative potentials are plotted to the right.[14] The current corresponding to

12 When a redox couple is present at each electrode and there are no contributions from liquid junctions (yet to be discussed), the open-circuit potential is also the *equilibrium potential*. This is the situation for both cells in Figure 1.1.1.

13 In this case, one of the two electrodes is a genuine reference electrode, but this is not true in all two-electrode cells.

14 The convention of taking $i$ positive for a cathodic current stems from early work at Hg electrodes, where reduction reactions were usually studied. By making this choice and plotting negative potentials toward the right, it is possible to represent data in first-quadrant graphs. This convention has the drawback of having increasingly positive currents corresponding to increasingly negative potentials; therefore, it sometimes seems peculiar. Yet, it has continued among many practitioners, even though oxidation reactions are now studied quite commonly. The authors considered a change to the opposite convention for this edition, but have elected to retain the historical practice for two main reasons: (a) The literature was dominated for a long time by this convention, and most figures that we have taken from the literature follow it. (b) There is a pedagogical advantage in consistently writing half-cell reactions in the reductive direction, as we will see in Chapter 2. Even so, many practitioners prefer to take anodic current as positive and to plot positive potentials toward the right. When looking over a derivation in the literature or examining a published $i - E$ curve, it is important to recognize which convention is being used (i.e., "Which way is up?"). Given history and contemporary practice, one has no choice but to become versatile about these things.

the reduction of $H^+$ rises sharply as the potential of the Pt electrode approaches $E^0$ for the $H^+/H_2$ reaction (0 V *vs.* NHE or −0.07 V *vs.* the Ag/AgBr electrode). At any moment, that same current passes at the Ag/AgBr reference electrode, where it causes the oxidation of Ag in the presence of $Br^-$ in solution to form AgBr. The conservation of charge requires that the rate of oxidation at the Ag electrode be equal to the rate of reduction at the Pt electrode.[15]

When the potential of the Pt electrode is made sufficiently positive, electrons are drawn from the solution phase into the electrode, as $Br^-$ is oxidized to $Br_2$ (and $Br_3^-$). The corresponding oxidation (*anodic*) current increases sharply (in the negative direction) as $E_{Pt}$ approaches $E^0$ for the half-reaction,

$$Br_2 + 2e \rightleftharpoons 2Br^- \tag{1.1.18}$$

which is +1.09 V *vs.* NHE or +1.02 V *vs.* Ag/AgBr. As this reaction occurs (right-to-left) at the Pt electrode, AgBr in the reference electrode is reduced to Ag, and $Br^-$ dissolves into solution.

Figure 1.1.5 is an example of a *background i − E curve*, depicting the behavior of a working electrode immersed in a solution containing only an electrolyte added to decrease the solution resistance (a *supporting electrolyte*). Background curves generally feature sharply rising currents on either side, because the corresponding reactants are present at high concentrations (e.g., $H^+$ on the negative side and $Br^-$ on the positive side, in the case of Figure 1.1.5). At some extreme potential (relative to the zero-current potential), a background current becomes so great that it obscures any smaller currents from parallel electrode reactions (perhaps from species of interest added to the blank electrolyte for investigation). A *background limit* is a potential beyond

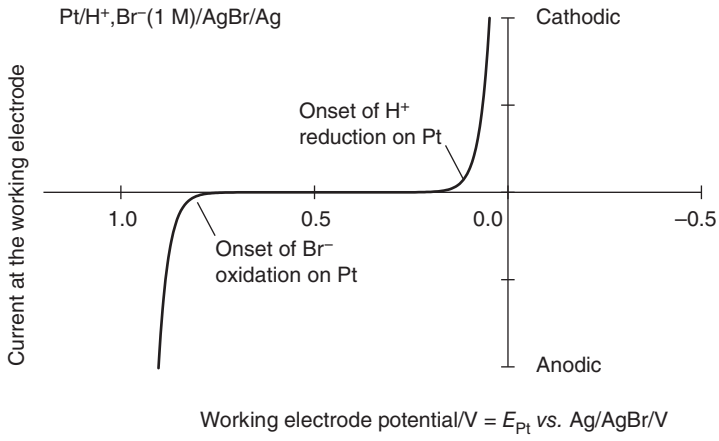



**Figure 1.1.5** Current–potential curve for the Pt working electrode in Pt/$H^+$(1 M), $Br^-$(1 M)/AgBr/Ag, showing proton reduction and bromide oxidation. Since $E_{Ag/AgBr} = 0.07$ V *vs.* NHE, the potential axis could be converted to $E_{Pt}$ *vs.* NHE by adding 0.07 V to each value of potential. The reader may expect the rise in reductive current to be closer to 0.0 V *vs.* NHE (−0.07 V on the scale used here). Because the proton concentration is so large, the hydrogen discharge wave is enormous. On the observed current scale, one sees only the very "foot" of that wave, which is significantly positive of 0.0 V *vs.* NHE. This effect applies to many processes determining background limits.

15 Although the flow of current in the cell will cause chemical conversion of some Ag + $Br^-$ into AgBr or *vice versa*, the amounts of reaction are typically very small and will not appreciably change the bulk concentration of $Br^-$. Also, the reference electrode is often made significantly bigger than the working electrode and is sealed off from the working electrode with an ionically conducting barrier, such as a frit or a fiber. These precautions give the reference electrode an ability to accept the passage of modest current with negligible overall compositional change and to avoid contamination from the working side of the cell.

which useful information usually cannot be obtained. The *working range* (or *potential window*) is the region between the positive and negative background limits, where reactions other than the background processes can be studied, given the electrode material, solvent, and supporting electrolyte. In the system of Figure 1.1.5, the working range is roughly from +0.9 to +0.1 V.

The open-circuit potential (i.e., the zero-current potential) is not well defined in Figure 1.1.5. One can say only that it lies somewhere between the background limits. The value found experimentally will depend upon trace impurities in the solution (e.g., oxygen) and the previous history of the Pt electrode.

***(c) A Change of Working Electrode***

Let us now consider the same cell, but with the Pt replaced with a mercury working electrode:

$$\mathrm{Hg/H^+(1\ M), Br^-(1\ M)/AgBr/Ag} \tag{1.1.19}$$

We still cannot calculate an open-circuit potential for the cell, because we cannot define a redox couple for the Hg electrode. Upon examining the behavior of this cell with an applied external potential, we find that the electrode reactions and the observed current–potential behavior are very different from the earlier case. The results are depicted in Figure 1.1.6, showing the current at the Hg working electrode *vs.* the potential of that electrode, measured with respect to the reference and then shifted to the NHE scale.

When the potential of the Hg is made negative, there is essentially no cathodic current in the region near 0.0 V, where thermodynamics predict that $H_2$ evolution should occur. Indeed, the potential must be brought to considerably more negative values, as shown in Figure 1.1.6, before this reaction takes place. The thermodynamics have not changed, for the equilibrium potential of half-reaction 1.1.7 is independent of the metal electrode [Section 2.2.4(*e*)]. However, when mercury serves as the electrode for the hydrogen evolution reaction, the reaction rate (characterized by a *heterogeneous rate constant*) is much lower than at Pt. Under these circumstances, the reaction does not occur at values suggested by thermodynamics. Considerably higher electron energies (corresponding to more negative potentials) must be applied to make the reaction occur at a measurable rate.

The rate constant for a heterogeneous electron-transfer reaction is a function of applied potential. Any additional potential (beyond the thermodynamic requirement) needed to drive

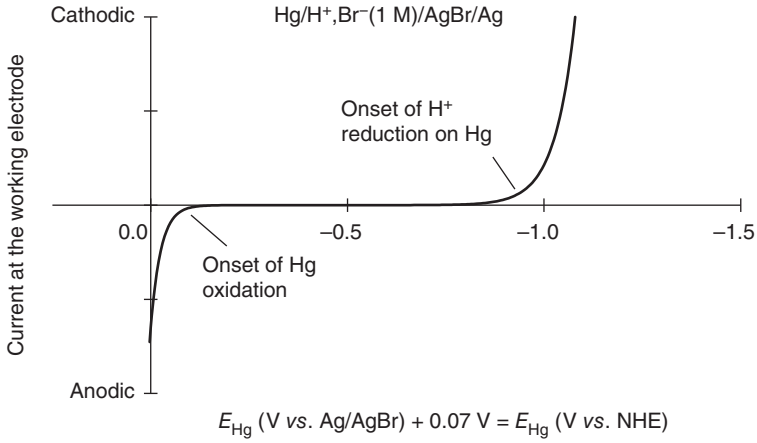



**Figure 1.1.6** Current–potential curve for the Hg electrode in the cell $Hg/H^+(1\ M), Br^-(1\ M)/AgBr/Ag$, showing the limiting processes: proton reduction with a large negative overpotential and mercury oxidation. The potential axis is defined through the process outlined in the caption to Figure 1.1.5.

a reaction at a certain rate is called an *overpotential*; thus, it is said that mercury shows "a high overpotential for the hydrogen evolution reaction." Chapter 15 covers this reaction in detail and provides an explanation for the behavior at mercury. As we will see in Chapter 3, an overpotential has the effect of lowering the activation barrier for an electrode reaction.

When the mercury is brought to more positive potentials, both the anodic reaction and the potential range for flow of current differ from those observed when Pt is used as the electrode. The positive background limit occurs when Hg is oxidized to $Hg_2Br_2$ at a potential near 0.14 V *vs*. NHE (0.07 V *vs*. Ag/AgBr), characteristic of the half-reaction

$$Hg_2Br_2 + 2e \rightleftharpoons 2Hg + 2Br^- \tag{1.1.20}$$

As we can surmise from these two examples, background limits vary from system to system and depend generally upon the electrode material, the solvent, and the supporting electrolyte on the working side of the cell.

***(d) Addition of an Electroactive Solute***

Let us now move beyond background curves by considering the previous cell with the addition of a small amount of $Cd^{2+}$ to the solution,

$$Hg/H^+(1\ M), Br^-(1\ M), Cd^{2+}(10^{-3}\ M)/AgBr/Ag \tag{1.1.21}$$

This case exemplifies the addition of a species of interest to a blank electrolyte for electrochemical investigation.

The current–potential curve is shown in Figure 1.1.7. Note the appearance of a *reduction wave* at about −0.4 V *vs*. NHE arising from the reduction reaction

$$CdBr_4^{2-} + 2e \xrightarrow{Hg} Cd(Hg) + 4Br^- \tag{1.1.22}$$

where Cd(Hg) denotes cadmium amalgam (i.e., with Cd atoms dissolved in the Hg). The shape and height of such a wave will be covered in Section 1.3.2.[16]

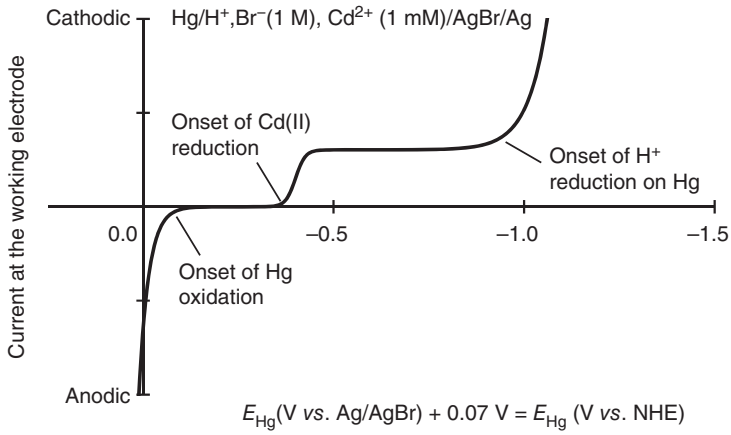



**Figure 1.1.7** Current–potential curve for the Hg working electrode in the cell $Hg/H^+(1\ M), Br^-(1\ M), Cd^{2+}(10^{-3}\ M)/AgBr/Ag$, showing a reduction wave for Cd(II) between −0.3 and −0.5 V. Potentials have been converted to the NHE scale in the manner identified in the caption to Figure 1.1.5.

16 If $Cd^{2+}$ were added to the cell in Figure 1.1.4 and a current–potential curve taken, the result would be essentially the same as in Figure 1.1.5, found in the absence of $Cd^{2+}$. At a Pt electrode, proton reduction occurs at less negative potentials than are required for the reduction of Cd(II), so the cathodic background limit occurs in 1 M HBr far before the cadmium reduction wave can be seen.

***(e) Precedence of Electrode Reactions***

When the potential of an electrode is moved from its open-circuit value toward more negative potentials, the substance that will be reduced first (assuming all possible electrode reactions have fast kinetics) is the oxidant in the couple with the least negative (or most positive) $E^0$. For example, consider Figure 1.1.8*a*, which relates to a platinum electrode immersed in an aqueous solution containing 0.01 M each of $Fe^{3+}$, $Sn^{4+}$, and $Ni^{2+}$ in 1 M HCl. The first substance reduced will be $Fe^{3+}$, since the $E^0$ of this couple is most positive.

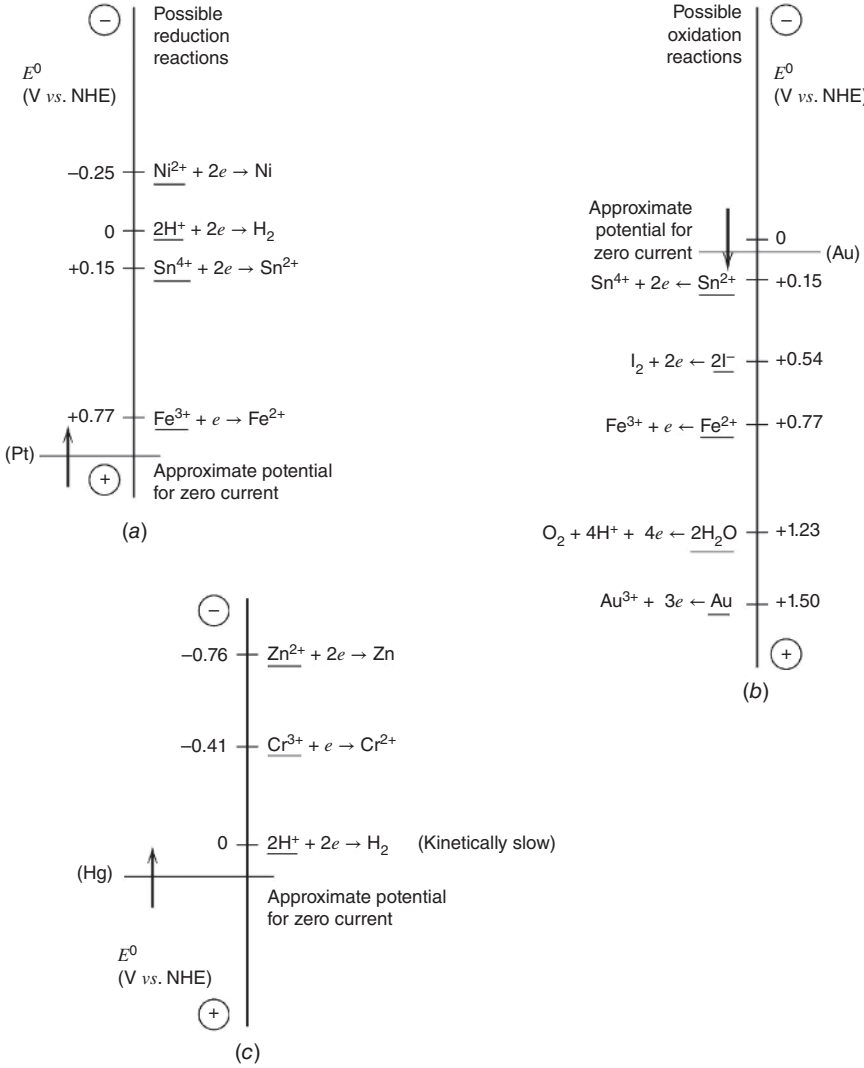



**Figure 1.1.8** (*a*) Potentials for possible reductions at a platinum electrode, initially at ~1 V *vs*. NHE in a solution of 0.01 M each of $Fe^{3+}$, $Sn^{4+}$, and $Ni^{2+}$ in 1 M HCl. (*b*) Potentials for possible oxidation reactions at a gold electrode, initially at ~0.1 V *vs*. NHE in a solution of 0.01 M each of $Sn^{2+}$ and $Fe^{2+}$ in 1 M HI. (*c*) Potentials for possible reductions at a mercury electrode in 0.01 M $Cr^{3+}$ and $Zn^{2+}$ in 1 M HCl. The arrows indicate the directions of potential change discussed in the text. Potentials are plotted with the negative direction upward, because this direction corresponds with increasing energy of the available electrons on the electrode (Sections 1.1.4 and 2.2.5). Plotting potentials in $i - E$ curves with the negative direction to the right is consistent with this consideration.

Likewise, when the potential of the electrode is moved from its open-circuit value toward more positive potentials, the substance that will be oxidized first is the reductant in the couple of least positive (or most negative) $E^0$. Thus, for a gold electrode in an aqueous solution containing 0.01 M each of $Sn^{2+}$ and $Fe^{2+}$ in 1 M HI (Figure 1.1.8*b*), the $Sn^{2+}$ will be first oxidized, since the $E^0$ of this couple is least positive.

One must remember, however, that these predictions are based on thermodynamic considerations (i.e., reaction energetics). Slow kinetics might prevent an electrode reaction from occurring at a significant rate in a potential region where the standard potential suggests that the reaction is possible. For a mercury electrode immersed in a solution of 0.01 M each of $Cr^{3+}$ and $Zn^{2+}$ in 1 M HCl (Figure 1.1.8*c*), the first reduction process predicted is the evolution of $H_2$ from $H^+$. As discussed earlier, this reaction is very slow on mercury, so the first process actually observed is the reduction of $Cr^{3+}$.

None of the cases in Figure 1.1.8 involves a redox couple for which both redox forms are present; consequently, there is no equilibrium defining the open-circuit potential of the electrode. In every electrochemical system, the open-circuit potential lies between the easiest oxidation and the easiest reduction. If, apart from species defining the background limits, the solution contains only oxidized forms eligible for reduction (as in Figure 1.1.8*a*,*c*), the open-circuit potential must lie between the positive background limit and the standard potential for the first electroreduction. If the solution contains only reduced forms eligible for oxidation (as in Figure 1.1.8*b*), the open-circuit potential must lie between the negative background limit and the standard potential for the first electrooxidation.

#### *(f) Both Redox Forms of a Couple as Solutes*

In some systems, both redox forms of a couple are present as solutes, and the behavior differs notably from the cases we have been discussing. Suppose, for example, that we make three changes in the cell of Figure 1.1.4:

- Employing a silver electrode covered with AgCl, rather than one covered with AgBr.
- Adopting a vessel having two compartments, one for each electrode, separated internally by a frit.
- Placing 1 M HCl in each compartment, but also including 2 mM Fe(II) and 4 mM Fe(III) in the solution at the Pt electrode.

Thus, the cell becomes

$$\mathrm{Pt/H^+(1\ M), Cl^-(1\ M), Fe(III)\ (4\ mM), Fe(II)\ (2\ mM)//H^+(1\ M), Cl^-(1\ M)/AgCl/Ag} \tag{1.1.23}$$

The compartments are employed to keep Fe(III) species away from the silver electrode, where they would otherwise react by oxidizing the metal. The frit prevents bulk mixing of the solutions in the two compartments, but allows them to remain in ionic electrical contact.

In this system, the silver electrode becomes an Ag/AgCl reference,[17] and the cell potential is the potential of the Pt working electrode against that reference, which can be re-expressed on the NHE scale, essentially as was done for Figures 1.1.6 and 1.1.7.

The iron species exist in 1 M HCl as chloro complexes, so we simply write the relevant couple as[18]

$$\mathrm{Fe(III)} + e \rightleftharpoons \mathrm{Fe(II)} \qquad E^{0\prime} = +0.70\ \mathrm{V}\ \textit{vs.}\ \mathrm{NHE\ (1\ M\ HCl)} \tag{1.1.24}$$

17 Although with 1 M HCl, rather than the usual case of saturated KCl.

18 In this case, we use a medium-specific *formal potential*, $E^{0\prime}$ rather than the standard potential, $E^0$, because of the complexation that takes place. Chapter 2 explains formal potentials. For now, just regard the formal potential as functionally the same as the standard potential.

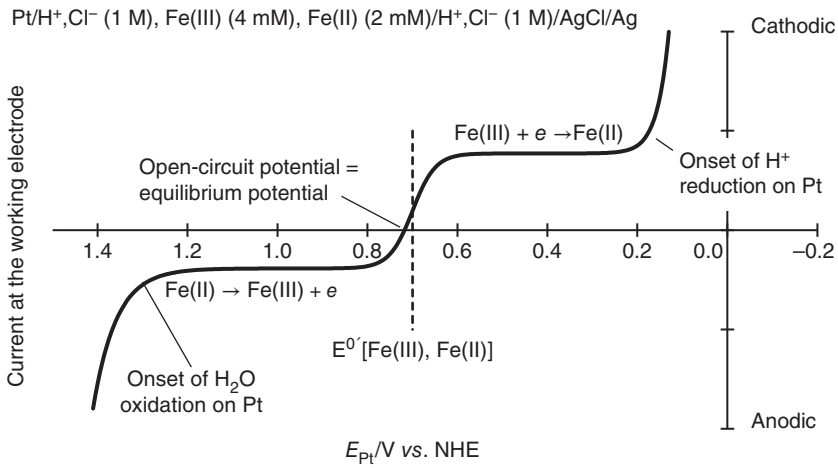



**Figure 1.1.9** Current–potential curve for a Pt working electrode in a system in which both Fe(III) and Fe(II) are present in the working solution. Cell configuration identified at top. A composite wave exists in which Fe(III) is reduced on the negative side of the open-circuit potential and Fe(II) is oxidized on the positive side.

Because the Pt electrode is in contact with both redox forms, the working electrode is poised by the Fe(III)/Fe(II) and shows a true equilibrium potential near $E^{0'}$ for (1.1.24). The current–potential curve is depicted in Figure 1.1.9.

As the potential moves negatively from the open-circuit potential, reduction of Fe(III) is immediately possible, because the open-circuit potential is already in the range of $E^{0'}$ for the couple. At open circuit (zero current), there is a dynamic equilibrium. The redox process proceeds in both directions [Fe(III) being reduced and Fe(II) being oxidized], but the rates are balanced and there is no net current. Negative movement of the potential away from the equilibrium value unbalances the rates to give a net cathodic current. Likewise, as the potential moves positively from the open-circuit value, net oxidation of Fe(II) is immediately possible.

The overall result is a composite wave for the Fe(III)/Fe(II) couple having both anodic and cathodic components, spanning $E^{0'}$. It is important to understand the essential continuity of oxidation and reduction for a given electrode process. We will emphasize it repeatedly in Section 1.3.2(*b*), in Chapters 3 and 5, and elsewhere.

Through these simple examples, we have seen that current–potential curves have many features in common with spectra arising from various forms of spectroscopy. In the most general terms, spectra represent the probability of a transition *vs*. the energy of a probing photon, and they are marked by features that can be exploited for qualitative identification, quantitative determination, or diagnosis of behavior. Current–potential curves represent the rate and direction of reaction at a working electrode *vs*. the energy of transferable electrons on that electrode, and they are also marked by features that can be exploited toward the same ends. Like spectra, current–potential curves are reflective of the electronic structures of participants; but unlike most spectra, they are essentially kinetic in basis. One must understand the contributing dynamics in the relevant electrode reactions to understand the curves fully. Current–potential curves arise from many different electrochemical methods, and we will be working constantly with them.

### 1.1.8 Control of Current *vs*. Control of Potential

Our work with $i-E$ curves is already substantial enough to suggest that there is a functional relationship between current and potential in electrochemical systems. Dictating one of these

variables determines the other, if experimental conditions otherwise remain constant. If one chooses to control the potential of the working electrode, for example, then the reaction energetics become defined by that election. The reaction rate and its time dependence (and, thus, the current and its time dependence) follow as consequences. Alternatively, one can choose to control the current, defining the reaction rate at the working electrode. Then, the energetics follow, as does the potential–time function.

There is an analogy with the behavior of homogeneous reactions, for which one can vary rate with temperature. However, one cannot control both reaction rate and reaction temperature under otherwise constant conditions. If one wants a given rate, one must accept the required temperature *vs*. time. Or if one wants to operate at a given temperature, one must accept the reaction rate *vs*. time.

Newcomers to electrochemistry often miss the point that current and potential cannot be controlled simultaneously in experimental systems, unless some other important variable, such as temperature, can change at the same time.

### 1.1.9 Faradaic and Nonfaradaic Processes

Two distinct classes of processes occur at electrodes. The more familiar group comprises reactions like those we have been discussing, in which electrons are transferred, oxidation or reduction happens, and charge moves across the electrode/solution interface. These events are stoichiometric and are governed by Faraday's law; thus, they are called *faradaic processes*. Electrodes at which faradaic processes occur are sometimes called *charge-transfer electrodes*.

We have also seen that a given electrode/solution interface can show a range of potentials where no charge-transfer reactions occur, because all such reactions are thermodynamically or kinetically unfavorable (e.g., the region in Figure 1.1.6 between −0.2 V and −0.8 V *vs*. NHE). However, the distribution of ions at the electrode/solution interface does change with changing potential or solution composition. Events at the electrode surface that do not involve charge transfer are called *nonfaradaic*. Even though charge does not cross the interface, nonfaradaic processes can cause external currents to flow, at least transiently, when the potential, electrode area, or solution composition changes. In studies focused on the nature of the electrode/solution interface, nonfaradaic processes can become the primary concern.

For now, we will continue to focus on faradaic processes, but in Section 1.6, we will discuss systems in which only nonfaradaic processes occur.

## 1.2 Faradaic Processes and Factors Affecting Rates of Electrode Reactions

### 1.2.1 Electrochemical Cells—Types and Definitions

Electrochemical cells in which faradaic currents are flowing are classified as either *galvanic* or *electrolytic* cells.

A *galvanic cell* is one in which reactions occur spontaneously at the electrodes when they are connected externally by a conductor (Figure 1.2.1*a*). These cells are often employed in converting chemical energy into electrical energy. Galvanic cells of commercial importance include *primary* (*nonrechargeable*) *cells* (e.g., the "alkaline" $Zn - MnO_2$ cell), *secondary* (*rechargeable*) *cells* (e.g., a charged $Pb - PbO_2$ storage battery or lithium-ion battery), and *fuel cells* (e.g., an $H_2 - O_2$ cell).

An *electrolytic cell* is one in which electrode reactions that would not occur spontaneously are driven by the imposition of an external voltage greater than the open-circuit potential of

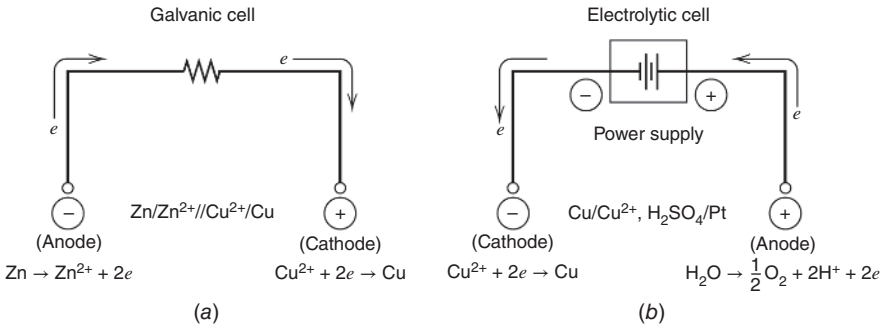



**Figure 1.2.1** (*a*) Galvanic and (*b*) electrolytic cells, both causing the plating of copper.

the cell (Figure 1.2.1*b*). These cells are frequently employed to carry out desired chemical reactions by expending electrical energy. Commercial processes involving electrolytic cells include electrolytic syntheses (e.g., the production of chlorine and aluminum), electrorefining (e.g., copper), and electroplating (e.g., silver and gold). The lead–acid storage cell (or any other secondary cell) is an electrolytic cell when it is being recharged, but is a galvanic cell when it is delivering power.

Although it is sometimes convenient to make a distinction between galvanic and electrolytic cells, we will most often be concerned with reactions occurring at only one of the electrodes. Treatment is simplified by concentrating our attention on only one-half of the cell at a time. If necessary, the behavior of a whole cell (i.e., whether galvanic or electrolytic) can be ascertained later by combining the characteristics of the individual half-cells.

The behavior of a single electrode and the fundamental nature of its reactions are independent of whether the electrode is part of a galvanic or electrolytic cell. For example, consider the cells in Figure 1.2.1. The reaction $Cu^{2+} + 2e \rightarrow Cu$ is the same in both cells. If one desires to plate copper, one could accomplish this either in a galvanic cell (using a counter half-cell with a more negative potential than that of $Cu^{2+}/Cu$) or in an electrolytic cell (using any counter half-cell and driving electrons to the copper electrode with an external power supply).

*Electrolysis* is a term that we define broadly to include chemical changes accompanying faradaic reactions at electrodes in contact with electrolytes. In discussing cells, one calls the electrode at which reductions occur the *cathode*, and the electrode at which oxidations occur the *anode*. A current in which electrons cross the interface from the electrode to a species in solution is a *cathodic current*, while electron flow from a solution species into the electrode is an *anodic current*. In an electrolytic cell, the cathode is negative with respect to the anode; but in a galvanic cell, the cathode is positive with respect to the anode.[19]

### 1.2.2 The Electrochemical Experiment and Variables in Electrochemical Cells

An experimental investigation of electrochemical behavior consists of controlling certain variables of a cell and observing how other variables (usually current, potential, or concentration) vary with time or with the controlled variables. The parameters of importance in

19 Because a cathodic current and a cathodic reaction can occur at an electrode that is either positive or negative with respect to another electrode (e.g., a reference electrode), it is poor usage to associate the term "cathodic" or "anodic" with potentials of a particular sign. For example, one should not say, "The potential shifted in a cathodic direction," when what is meant is, "The potential shifted in a *negative* direction." The terms anodic and cathodic refer to electron flow or current direction, not to potential.

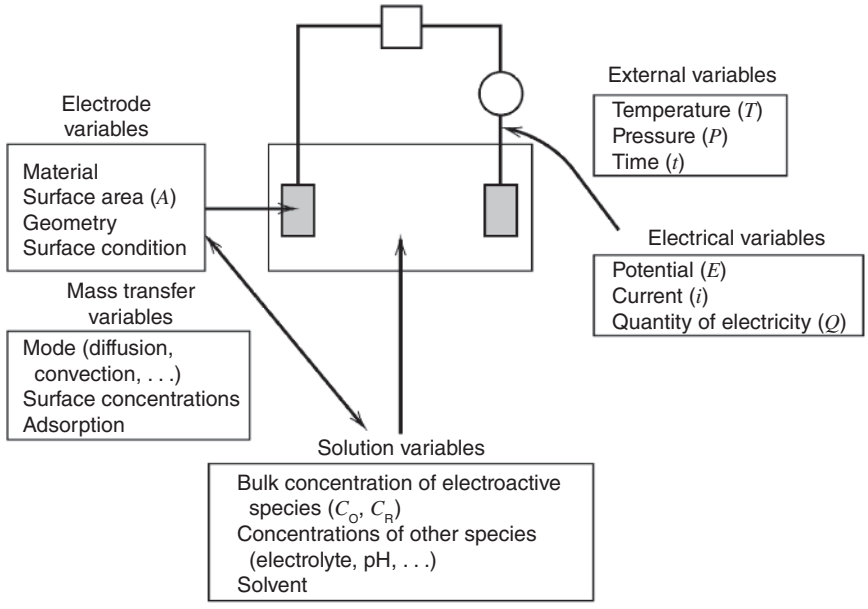



**Figure 1.2.2** Variables affecting the rate of an electrode reaction.

electrochemical cells are shown in Figure 1.2.2. Methods fall into broad categories; the following illustrate some of the differences in approach:

- In *potentiometry*, $i = 0$, and $E$ is determined as a function of concentration. Since no current flows in this experiment, no net faradaic reaction occurs, and the potential is frequently (but not always) governed by the thermodynamic properties of the system. Many of the variables (electrode area, mass transfer, electrode geometry) do not affect the potential directly.
- In *voltammetry*, the potential is controlled (normally following a particular function of time), and the resulting current is measured as a function of potential.
- In *galvanostatic* experiments, the current is controlled (usually as a defined function of time) and the potential is followed *vs*. time.
- In *coulometry*, the potential is held constant at a value where an electrode reaction occurs, and one measures the total charge passed, usually by integrating the current.

Most electrochemical experiments can be described in terms of the way in which the system responds to a perturbation. A certain excitation function (e.g., a potential step) is applied, and a certain response function (e.g., the resulting variation of current with time) is measured, with all other system variables held constant (Figure 1.2.3). If the excitation is time dependent, the response typically will also be a function of time. Such approaches are called *transient methods*. Alternatively, the excitation might be constant or a very slowly changing function of time, and the response might be steady with time. Approaches based on this concept are called *steady-state methods*.

The aim of the experiment is to obtain information (thermodynamic, kinetic, analytical, etc.) from observations of excitation and response functions and a knowledge of appropriate models for the system. This same basic idea is used in many other types of investigation, such as circuit testing or spectrophotometric analysis. In spectrophotometry, the excitation function is light of different wavelengths; the response function is the fraction of light transmitted by the system at these wavelengths; the system model is Beer's law or a molecular model; and the

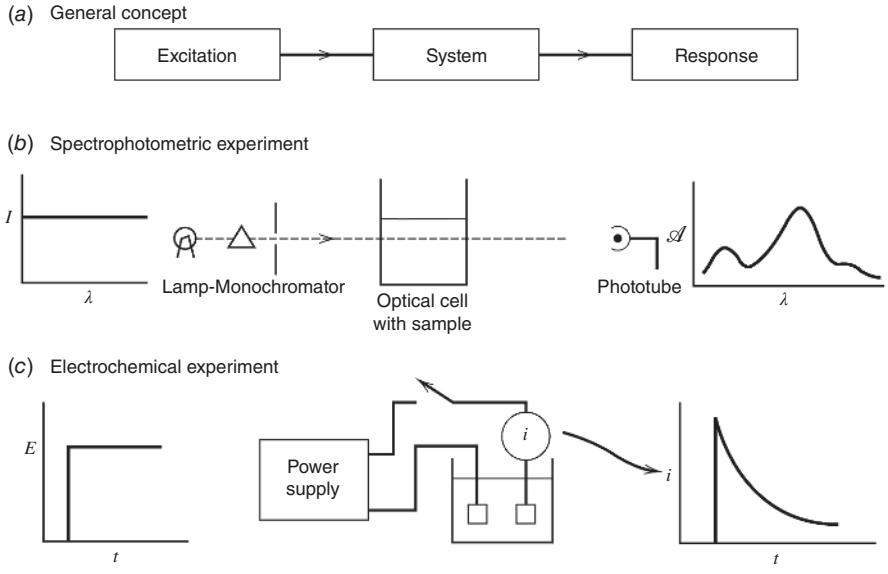



**Figure 1.2.3** (*a*) General principle of studying a system by application of an excitation (or perturbation) and observation of response. (*b*) In a spectrophotometric experiment, the excitation is light of different wavelengths ($\lambda$), and the response is the absorbance ($\mathcal{A}$) curve. (*c*) In an electrochemical potential step experiment, the excitation is the application of a potential step, and the response is the observed $i - t$ curve.

information content includes the concentrations of absorbing species, their absorptivities, or their transition energies.

Before developing some models for electrochemical systems, let us examine more closely the nature of the current and potential in an electrochemical cell. Consider Figure 1.2.4, in which a cadmium electrode immersed in 1 M $Cd(NO_3)_2$ is coupled to an SCE. The open-circuit potential of the cell is 0.64 V, with the copper wire attached to the cadmium electrode being

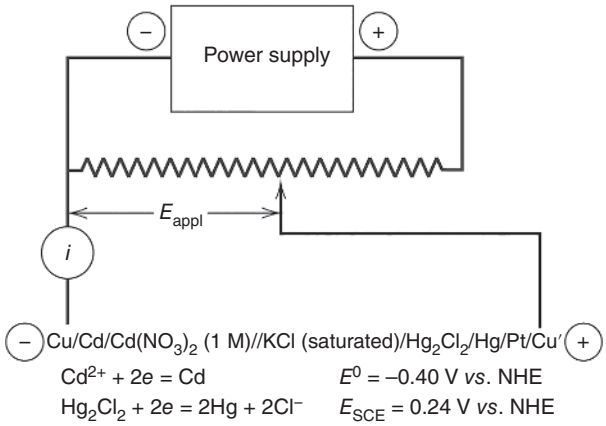



**Figure 1.2.4** Schematic cell connected to an external power supply. The resistor with an adjustable intermediate contact is called a *potentiometer*. The double slash in the cell notation indicates an interface between two different electrolytes (a *liquid junction*) with a negligible potential difference. To avoid contamination of the mercury pool in the SCE by dissolved copper, Pt is used as intermediate contact.

negative with respect to that attached to the mercury electrode.[20] When the voltage applied by the external power supply, $E_{appl}$, is 0.64 V, it exactly cancels the cell's open-circuit potential. There is no net driving force for the movement of charge, so $i = 0$. When $E_{appl}$ is made larger (i.e., $E_{appl} > 0.64$ V, such that the cadmium electrode is made even more negative with respect to the SCE), the power supply can drive electrons into the cadmium and withdraw them at the mercury. At the cadmium electrode, the reaction $Cd^{2+} + 2e \rightarrow Cd$ occurs, while at the SCE, mercury is oxidized to $Hg_2Cl_2$. The cell is electrolytic; the power supply is overcoming the spontaneous driving force of the cell. A question of interest might be: "If $E_{appl} = 0.80$ V (i.e., if the potential of the cadmium electrode is made −0.80 V *vs*. the SCE), what current will flow?" As we learned in Section 1.1.5, the question "What is $i$?" is, for this system, essentially the same as "What is the rate of the reaction, $Cd^{2+} + 2e \rightarrow Cd$?"

Information about an electrode reaction is often gained by determining the current at the working electrode as a function of potential, i.e., by obtaining $i-E$ curves. Certain terms are sometimes associated with features of the curves.[21] If a working electrode has a defined equilibrium potential, $E_{eq}$, that potential is an important reference point [Section 1.1.7(*a*)]. The departure of the electrode potential from the equilibrium value upon passage of faradaic current is termed *polarization*, which is measured by the *overpotential*, $\eta$,[22]

$$\eta = E - E_{eq} \tag{1.2.1}$$

Current–potential curves, particularly those obtained under steady-state conditions, are sometimes called *polarization curves*.

An *ideally nonpolarizable electrode* (INE) is an electrode whose potential does not change upon passage of current, i.e., an electrode of fixed potential.[23,24] Ideal nonpolarizability is characterized by a vertical region on an $i-E$ curve (Figure 1.2.5*a*). An SCE constructed with a sizable mercury pool would approach ideal nonpolarizability for small currents.

In contrast, an *ideally polarizable electrode* (IPE) shows a very large change in potential upon the passage of an infinitesimal current; thus, ideal polarizability is characterized by a horizontal, zero-current $i-E$ curve (Figure 1.2.5*b* and Section 1.6.1).

### 1.2.3 Factors Affecting Electrode Reaction Rate and Current

Consider an overall electrode reaction, $O + ne \rightleftharpoons R$, composed of a series of steps that cause the conversion of the dissolved oxidized species, O, to a reduced form, R, also in solution

20 This value is calculated from the Nernst equation using the information in Figure 1.2.4. The experimental value would also include the effects of activity coefficients and the liquid junction potential, which are neglected here. See Chapter 2.

21 These terms are carryovers from history and do not always represent the best possible terminology. However, their use is so ingrained in electrochemical jargon that it seems wisest to keep them and to define them as precisely as possible.

22 In the electrochemical literature, the term *polarization* describes the departure of an electrode from some reference point, but not always from an equilibrium potential. *Overpotential* is the measure of polarization relative to the chosen reference point.

23 An INE is also known as an *ideally depolarized electrode* (IDE). A substance is called a *depolarizer* if it causes an electrode to operate at a less extreme potential (i.e., to be nearer to its zero-current value) by virtue of being oxidized or reduced. Thus, ideal depolarization would yield the $i-E$ curve in Figure 1.2.5*a*.

24 The term *depolarizer* is also frequently used to denote a substance that is preferentially oxidized or reduced, to prevent an undesirable electrode reaction. Sometimes, it is simply another name for an electroactive substance.

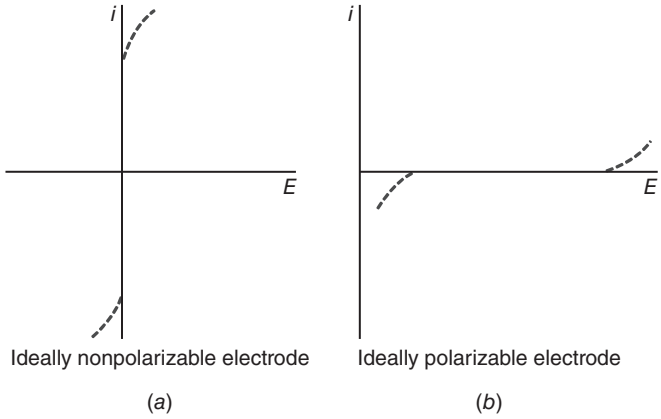



**Figure 1.2.5** Current–potential curves for (*a*) INE and (*b*) IPE. Dashed lines show behavior of actual electrodes that approach ideal behavior over limited ranges of current or potential. Departures from ideality in (*a*) reflect limitations in the kinetics of the electrode reaction. In (*b*), they arise from the onset of new electrode reactions.

(Figure 1.2.6). In general, the current (or electrode reaction rate) is governed by the rates of processes such as (1, 2):

- Mass transfer (e.g., of O from the bulk solution[25] to the electrode surface).
- Electron transfer at the electrode surface.

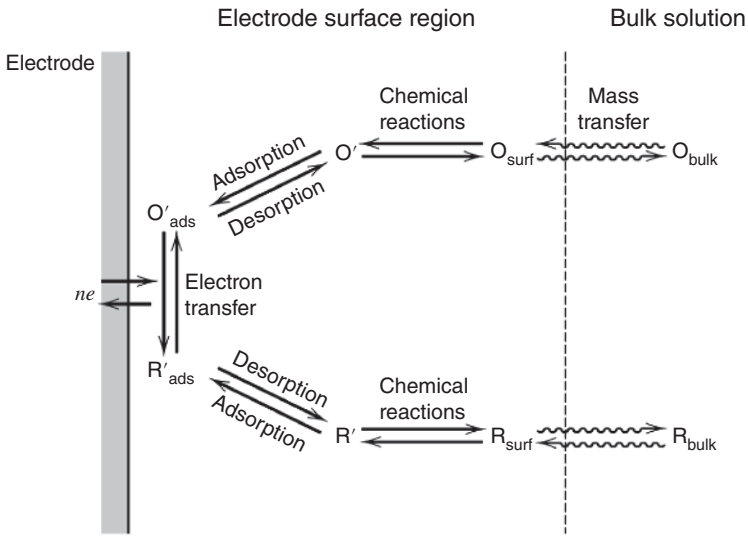



**Figure 1.2.6** Pathway of a general electrode reaction.

25 The *bulk solution* (often just called the *bulk*) is the body of solution sufficiently far from an electrode to have uniform composition at all points and, therefore, no gradient in concentration driven by processes at the electrode. Near the electrode, electroreactants are consumed and electroproducts are generated, so concentration gradients exist and are important. On a lab scale, the bulk is not very far from an electrode, typically less than a few hundred micrometers away. In many experiments, the bulk remains essentially unaffected by the electrode process; however, one cannot assume that it is always unaffected. Cells with large electrodes and efficient mass transfer can have the purpose of transforming the whole system, especially if the goal is to synthesize a product electrolytically. Systems built for "bulk electrolysis" are discussed in Chapter 12.

- Chemical reactions preceding or following the electron transfer. These might be homogeneous processes (e.g., protonation or dimerization) or heterogeneous reactions on the electrode surface (e.g., catalytic decomposition).
- Other surface reactions, such as adsorption, desorption, or crystallization.

The rate constants for some of these processes (e.g., electron transfer at the electrode surface or adsorption) depend upon the potential.

The simplest reactions involve only mass transfer of a reactant to the electrode, heterogeneous electron transfer involving nonadsorbed species, and mass transfer of the product to the bulk solution. A representative reaction of this sort is the reduction of the aromatic hydrocarbon 9,10-diphenylanthracene (DPA; Figure 1) to the radical anion ($DPA^{\bullet-}$) in an aprotic solvent [e.g., *N,N*-dimethylformamide (DMF)]. More complex reaction sequences are quite common. They may involve almost any kind of chemistry, including a series of electron transfers, coupling reactions in solution, protonations, branching mechanisms, parallel paths, or modifications of the electrode surface.

It is possible in several ways to obtain steady-state currents, and we will concentrate on such situations in Sections 1.3 and 1.4. When there is a steady current, the rates of all reaction steps in a mechanistic series are the same. The magnitude of this current is often limited by the inherent sluggishness of one or more processes called *rate-determining steps*. The more facile steps are held back from their maximum rates by the slowness with which a rate-determining step disposes of their products or delivers their reactants.

Each value of current is driven by a certain overpotential, $\eta$, which can be considered as a sum of terms associated with the different reaction steps: $\eta_{mt}$ (the *mass-transfer overpotential*), $\eta_{ct}$ (the *charge-transfer overpotential*), $\eta_{rxn}$ (the overpotential associated with a preceding reaction), *etc*. The overpotential of any step is an expression of how the applied electrical energy activates that step to operate at the rate required to deliver the given current density. Since $-\eta/i$ has units of resistance, the electrode reaction can be represented by an overall resistance, $R$, composed of a series of resistances representing the various steps: $R_{mt}$, $R_{ct}$, *etc*. (Figure 1.2.7). A kinetically facile, easily driven reaction step is characterized by a small resistance, while a sluggish step is represented by a high resistance.[26]

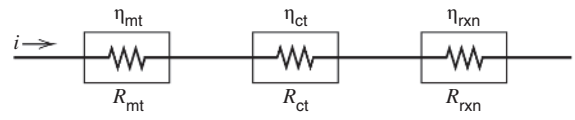



**Figure 1.2.7** Processes in an electrode reaction represented as resistances.

## 1.3 Mass-Transfer-Controlled Reactions

Let us now become more quantitative about the sizes and shapes of current–potential curves. We must be able to describe the rate of reaction at the electrode surface if we are to understand *i*.

In the simplest electrode reactions, the participants are chemically stable, and the rates of all associated chemical reactions are very rapid compared to those of the mass-transfer processes.

26 More accurately, what we have labeled as resistances should be considered as impedances. However, these impedances are functions (often very strong functions) of *E* or *i*, unlike the analogous ideal electrical elements. Typically, linear models like Figure 1.2.7 apply quantitatively only for very small perturbations about the equilibrium point, i.e., only when a *small signal* is applied.

We will find in Chapters 3 and 5 that if an electrode reaction involves only fast heterogeneous charge-transfer kinetics and mobile, reversible homogeneous reactions, then

- The homogeneous reactions can be regarded as being at equilibrium.
- The *surface concentrations* of species involved in the faradaic process are related to the electrode potential by an equation of the Nernst form.

Such electrode reactions are called *reversible* or *nernstian*, because the principal species obey thermodynamic relationships at the electrode surface.

In nernstian systems, the net rate of the electrode reaction is governed totally by the rate at which the electroreactant is brought to the surface by mass transfer, $\upsilon_{mt}$ (mol cm$^{-2}$ s$^{-1}$). From (1.1.15),[27]

$$\upsilon_{mt} = \pm i/nFA \qquad (+ \text{ for a reduction}, \quad - \text{ for an oxidation}) \tag{1.3.1}$$

Since mass transfer plays a big role in electrochemical dynamics, we will next review its three modes and then consider mathematical methods for treating them.

### 1.3.1 Modes of Mass Transfer

Mass transfer—the movement of material from one location in solution to another—arises from differences in electrical or chemical potential at the two locations or from the physical movement of volume elements of solution. The modes of mass transfer, amplified in Chapter 4, are:

- *Migration*. Movement of a charged body under the influence of an electric field (a gradient of electrical potential).[28]
- *Diffusion*. Movement of a species under the influence of a gradient of chemical potential (i.e., a concentration gradient).
- *Convection*. Stirring or hydrodynamic transport. Fluid flow occurs because of natural convection (convection caused by density gradients) and forced convection, and is characterized by stagnant regions, laminar flow, and turbulent flow.

Mass transfer to an electrode surface is governed by the *Nernst–Planck equation*, written in the following way for one-dimensional mass transfer along the $x$-axis, normal to the surface,

$$\boxed{J_j(x) = -D_j \frac{\partial C_j(x)}{\partial x} - \frac{z_j F}{RT} D_j C_j(x) \frac{\partial \phi(x)}{\partial x} + C_j(x)\upsilon(x)} \tag{1.3.2}$$

where $J_j(x)$ is called the *flux* of species $j$ (mol s$^{-1}$ cm$^{-2}$) at distance $x$ from the surface. This is the net rate at which the species crosses a unit area at $x$. A positive flux describes net movement toward greater $x$. In this equation, $D_j$ is the diffusion coefficient (cm$^2$/s); $\partial C_j(x)/\partial x$ is the concentration gradient at distance $x$; $\partial\phi/\partial x$ is the potential gradient; $z_j$ and $C_j$ are the charge (dimensionless) and concentration (mol/cm$^3$) of species $j$, respectively; and $\upsilon(x)$ is the velocity (cm/s) with which a solution volume element at $x$ translates along the axis. The Nernst–Planck equation is derived and discussed in Chapter 4. The three terms on the right side represent the contributions of diffusion, migration, and convection to the flux.

The flux of species $j$ at the electrode surface, $J_j(x = 0)$, has a special interpretation. If it is negative, then it describes a flux into the surface and must be understood chemically as the rate

27 $\upsilon_{mt}$ is an unsigned quantity. The explicit signs in (1.3.1) are in recognition that the current is positive for a reduction and negative for an oxidation.

28 Sometimes called *drift*.

at which species *j* is consumed by electrolysis. If positive, it describes a flux out of the surface and, therefore, the rate at which species *j* is produced by the electrode reaction. If it is zero, then species *j* is neither a reactant nor a product of the electrode reaction.

Suppose species *k* is the only electroreactant. We can identify the flux magnitude $|J_k(x=0)|$ as $\upsilon_{mt}$ in (1.3.1), from which we obtain,

$$\frac{|i|}{nFA} = |J_k(x=0)| \tag{1.3.3}$$

In later chapters, we will use the Nernst–Planck equation to calculate mass-transfer-limited currents for many different experimental circumstances. Computing the flux is complex when all three forms of mass transfer contribute; hence, electrochemical systems are often designed to render one or two of the contributions negligible. For example, the migrational component can be reduced to unimportance by adding an inert electrolyte (a *supporting electrolyte*) at a concentration much larger than that of the electroactive species (Section 4.3.2). Convection can be avoided by preventing stirring in the electrochemical cell. Alternatively, convection can be made dominant in a well-defined way by using a rotating disk electrode or a flow cell.

In the rest of this section, we present an approximate treatment of steady-state mass transfer, which will give insight into electrochemical reactions without elaborate mathematical detail.

### 1.3.2 Semiempirical Treatment of Steady-State Mass Transfer

Consider the reduction of a species O at a cathode, $O + ne \rightleftharpoons R$. In an actual case, the oxidized form, O, might be $Fe(CN)_6^{3-}$, and the reduced form, R, might be $Fe(CN)_6^{4-}$, but with only $Fe(CN)_6^{3-}$ initially present at the millimolar level in a solution of 0.1 M $K_2SO_4$. We envision a cell with a platinum working electrode and an SCE reference electrode, and we focus on conditions that produce steady-state mass transfer to the electrode surface.

An effective approach is to make the working electrode in the form of a disk embedded in an insulator and to rotate the assembly at a known rate about its central axis; this is a *rotating disk electrode* (RDE) and is discussed in Section 10.2. The rotation causes steady fluid flow upward along the axis of rotation, then radially outward from the face of the electrode because of centrifugal effects. It is characteristic of the RDE to deliver a steady current when the electrode is held at a potential where an electrochemical reaction can occur. If the potential is changed, the system will establish a new steady state after a brief transition.

Steady-state behavior can be obtained in other systems, too. The most important cases involve very small working electrodes shaped as spheres, hemispheres, or disks. These have radii from 25 μm to 10 nm and are known as *ultramicroelectrodes* (UME). Chapter 5 is wholly dedicated to steady-state experiments at UMEs. The basis for attaining a steady state at a UME is not as intuitive as at an RDE, so we concentrate now on the latter; however, the results derived here apply broadly to steady-state systems.

Once electrolysis begins at an RDE, species O is consumed at the electrode surface, so its surface concentration, $C_O(x=0)$, becomes smaller than the value in bulk solution, $C_O^*$. A *concentration profile* develops from the surface to the bulk, as shown by either of the solid curves in Figure 1.3.1. Stirring is ineffective near the electrode surface, so a stagnant layer (sometimes called the *Nernst diffusion layer*) extends outward for a thickness, $\delta_O$. Beyond $x = \delta_O$, convection is assumed to maintain the concentration at $C_O^*$ (dashed lines in Figure 1.3.1). Since there is an excess of supporting electrolyte, migration is not important anywhere.

Inside the diffusion layer ($x < \delta_O$), where neither convection nor migration are operative, the flux of O is given by the first (diffusive) term in (1.3.2). At the electrode surface,

$$J_O(x=0) = -D_O(dC_O/dx)_{x=0} \tag{1.3.4}$$

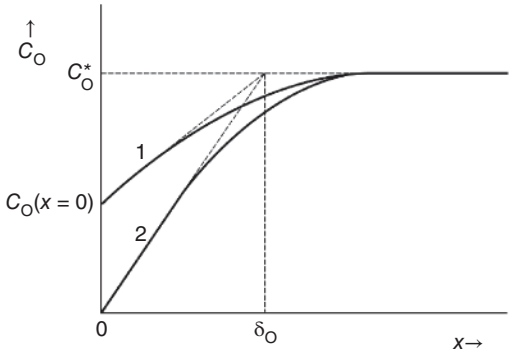



**Figure 1.3.1** Concentration profiles (solid lines) and diffusion-layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface, and $\delta_O$ is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (*1*) where $C_O(x = 0)$ is about $C_O^*/2$, (*2*) where $C_O(x = 0) \approx 0$ and $i = i_l$. When a system achieves steady state, the concentration profile remains steady, and the flux of O is the same at any plane.

If one further assumes a linear concentration gradient within the diffusion layer, then, from equation (1.3.4)

$$J_O(x = 0) = -D_O[C_O^* - C_O(x = 0)]/\delta_O \tag{1.3.5}$$

Since $\delta_O$ is often unknown, it is convenient to combine it with the diffusion coefficient as $m_O = D_O/\delta_O$, and to write equation (1.3.4) as

$$J_O(x = 0) = -m_O[C_O^* - C_O(x = 0)] \tag{1.3.6}$$

where the *mass-transfer coefficient*, $m_O$, has units of cm/s.[29]

From equations (1.3.3) and (1.3.6), with recognition that $i$ is positive for the reduction occurring at the electrode,

$$\boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]} \tag{1.3.7}$$

At the same time, R is produced at the electrode surface, so that $C_R(x = 0) > C_R^*$ (where $C_R^*$ is the bulk concentration of R). Therefore,

$$\boxed{\frac{i}{nFA} = m_R[C_R(x = 0) - C_R^*]} \tag{1.3.8}$$

For the case when $C_R^* = 0$ (no R in the bulk solution),

$$\boxed{\frac{i}{nFA} = m_R C_R(x = 0)} \tag{1.3.9}$$

The values of $C_O(x = 0)$ and $C_R(x = 0)$ depend on the electrode potential, $E$. The largest rate of mass transfer of O occurs when $C_O(x = 0)$ is driven to zero—or more precisely, when $C_O(x = 0) << C_O^*$, so that $C_O^* - C_O(x = 0) \approx C_O^*$. The value of the current under these conditions is called the *limiting current*, $i_l$, where

$$\boxed{i_l = nFAm_O C_O^*} \tag{1.3.10}$$

When the current reaches its limiting value, the electrode process is occurring at the maximum rate possible for a given set of mass-transfer conditions, because O is being reduced as fast as it can be brought to the electrode surface.

---

29 While $m_O$ is treated here as a phenomenological parameter, in more exact treatments the value of $m_O$ can sometimes be specified in terms of measurable quantities. For the rotating disk electrode (Section 10.2.2), $m_O = 0.62D_O^{2/3}\omega^{1/2}\nu^{-1/6}$ where $\omega$ is the angular velocity of the disk (i.e., $2\pi f$, with $f$ being the frequency in revolutions per second) and $\nu$ is the kinematic viscosity (i.e., viscosity/density, with units of $cm^2/s$). At a spherical UME of radius $r_0$, $m_O = D_O/r_0$. At a disk UME of radius $r_0$, $m_O = 4D_O/\pi r_0$ (Section 5.2.5).

Equations (1.3.7) and (1.3.10) can be combined to obtain expressions for $C_O(x = 0)$:

$$\boxed{\frac{C_O(x=0)}{C_O^*} = 1 - \frac{i}{i_l}} \tag{1.3.11}$$

$$C_O(x=0) = \frac{i_l - i}{nFAm_O} \tag{1.3.12}$$

Thus, the concentration of species O at the electrode surface is linearly related to the current and varies from $C_O^*$, when $i = 0$, to a negligible value, when $i = i_l$.

If the kinetics of interfacial electron transfer are rapid, the concentrations of O and R *at the electrode surface* can be assumed to be at equilibrium with the electrode potential, as governed by the Nernst equation for the half-reaction[30]

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O(x=0)}{C_R(x=0)} \tag{1.3.13}$$

We can derive the steady-state $i - E$ curves for this nernstian system under several different conditions.

***(a) R Initially Absent***

When $C_R^* = 0$, $C_R(x = 0)$ can be obtained from (1.3.9):

$$C_R(x=0) = i/nFAm_R \tag{1.3.14}$$

Then, combining equations (1.3.12)–(1.3.14), we obtain

$$\boxed{E = E^{0'} + \frac{RT}{nF} \ln \frac{m_R}{m_O} + \frac{RT}{nF} \ln \left( \frac{i_l - i}{i} \right)} \tag{1.3.15}$$

An $i - E$ plot is shown in Figure 1.3.2*a*. Note that when $i = i_l/2$,

$$\boxed{E = E_{1/2} = E^{0'} + \frac{RT}{nF} \ln \frac{m_R}{m_O}} \tag{1.3.16}$$

Thus,

$$\boxed{E = E_{1/2} + \frac{RT}{nF} \ln \left( \frac{i_l - i}{i} \right)} \tag{1.3.17}$$

The *half-wave potential*, $E_{1/2}$, is independent of the substrate concentration and is, therefore, characteristic of the O/R system. When $m_O$ and $m_R$ have similar values (as they often do), $E_{1/2}$ is within a few mV of $E^{0'}$.

When a system conforms to (1.3.17), a plot of $E$ *vs.* $\log[(i_l - i)/i]$ is a straight line with a slope of $2.3RT/nF$ (or $59.1/n$ mV at 25 °C). Alternatively (Figure 1.3.2*b*), $\log[(i_l - i)/i]$ *vs.* $E$ is linear with a slope of $nF/2.3RT$ (or $n/59.1$ mV$^{-1}$ at 25 °C) and has an $E$-intercept of $E_{1/2}$.

The limiting current is proportional to the bulk concentration of species O and can be used as the basis for analytical determinations, usually by calibration or standard addition.

With this simple example, we see that the position of the reversible wave on the potential axis is determined by the standard potential of the electrode reaction and that different features of the wave can provide access to chemical information, including $E_{1/2}$, $E^{0'}$, $C_O^*$, $m_O$, or $n$, depending on what might otherwise be known about the system.

---

30 Here we use $E^{0'}$, called the *formal potential*, rather than the standard potential, $E^0$. The formal potential is an adjusted form of the standard potential, manifesting activity coefficients and some chemical effects of the medium. In Section 2.1.7, it will be introduced in more detail. For the present it is not necessary to distinguish between $E^{0'}$ and $E^0$.

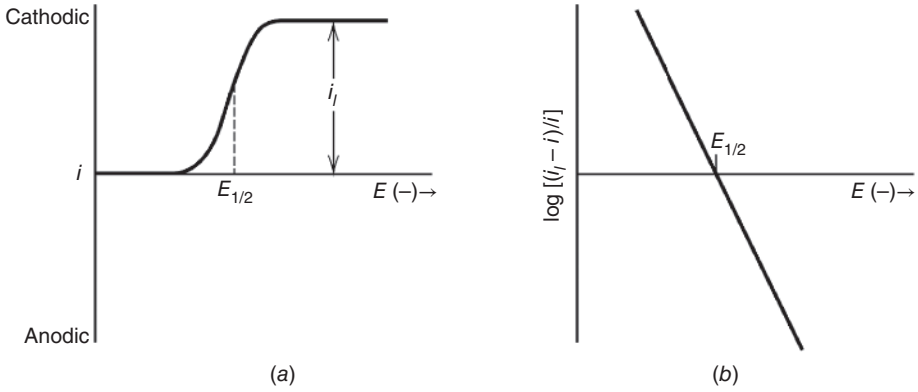



**Figure 1.3.2** (*a*) Current–potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (*b*) $\log[(i_l - i)/i]$ *vs*. *E* for this system.

***(b) Both O and R Initially Present***

When both members of the redox couple exist in the bulk, we must distinguish between a *cathodic limiting current*, $i_{l,c}$, when $C_O(x = 0) \approx 0$, and an *anodic limiting current*, $i_{l,a}$, when $C_R(x = 0) \approx 0$. We still have $C_O(x = 0)$ given by (1.3.12), but with $i_l$ now specified as $i_{l,c}$. The limiting anodic current reflects the maximum rate at which R can be brought to the electrode surface for conversion to O. It is obtained from (1.3.8):

$$\boxed{i_{l,a} = -nFAm_R C_R^*} \tag{1.3.18}$$

(The negative sign arises because of our convention that anodic currents are negative.) Thus, $C_R(x = 0)$ is given by

$$C_R(x = 0) = \frac{i - i_{l,a}}{nFAm_R} \tag{1.3.19}$$

$$\boxed{\frac{C_R(x = 0)}{C_R^*} = 1 - \frac{i}{i_{l,a}}} \tag{1.3.20}$$

The $i - E$ curve is then

$$\boxed{E = E^{0\prime} + \frac{RT}{nF} \ln \frac{m_R}{m_O} + \frac{RT}{nF} \ln \left( \frac{i_{l,c} - i}{i - i_{l,a}} \right)} \tag{1.3.21}$$

or

$$\boxed{E = E_{1/2} + \frac{RT}{nF} \ln \left( \frac{i_{l,c} - i}{i - i_{l,a}} \right)} \tag{1.3.22}$$

where $E_{1/2}$ is as defined in (1.3.16). It is the potential where the current is exactly halfway between the two limiting currents; i.e., when $i = (i_{l,c} + i_{l,a})/2$.

A plot of this equation is shown in Figure 1.3.3. When $i = 0$, $E = E_{eq}$ and the system is at equilibrium. Surface concentrations are then equal to the bulk values. When current flows, the potential deviates from $E_{eq}$, and the extent of this deviation is the mass-transfer overpotential. (An equilibrium potential is not defined for the O/R system when only one member of the redox couple is present, e.g., where $C_R^* = 0$ as in Figure 1.3.2.)

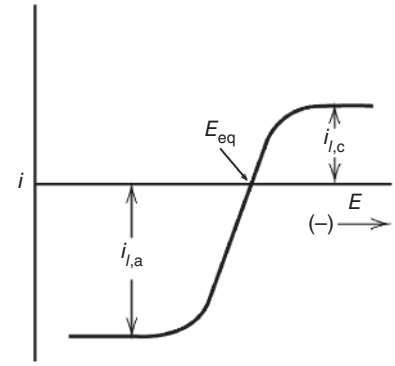



**Figure 1.3.3** Current–potential curve for a nernstian system involving two soluble species with both forms initially present.

The chemical information available from this wave is similar to that for the case without R initially present; however, there is more here, because $i_{l,a}$ and $i_{l,c}$ are independently informative. The anodic limiting current is proportional to $m_R C_R^*$; the cathodic limiting current, to $m_O C_O^*$.

Note that the reduction of O is not widely separated on the potential axis from the oxidation of R. The transition from one to the other is smooth, happening in a single wave. On the negative side of $E_{eq}$ (the zero-current potential), net reduction occurs. On the positive side, net oxidation. The whole wave is found in the region of $E^{0'}$ for the reaction. These are characteristics of reversible systems, for which kinetics are fast and mass transfer controls the response. [See also the discussion of the Fe(III)/Fe(II) couple in Section 1.1.7(*f*).] Many newcomers to electrochemistry acquire the notion that reduction and oxidation are separated widely on the potential axis, one near $E^{0'}$ and the other near $-E^{0'}$. It is important to avoid that mistaken idea.[31]

#### *(c) R Present as the Electrode Material*

Now suppose that species R is a metal, and the electrode reaction occurs on bulk R (e.g., $Ag^+ + e \rightleftharpoons Ag$). Usually R is at unit activity, [32] so the Nernst equation becomes

$$E = E^{0'} + \frac{RT}{nF} \ln C_O(x = 0) \tag{1.3.23}$$

Using the value of $C_O(x = 0)$ from equation (1.3.11),

$$\boxed{E = E^{0'} + \frac{RT}{nF} \ln C_O^* + \frac{RT}{nF} \ln \left( \frac{i_l - i}{i_l} \right)} \tag{1.3.24}$$

The corresponding current–potential curve is shown in Figure 1.3.4. When $i = 0$, $E = E_{eq} = E^{0'} + (RT/nF) \ln C_O^*$.

In Sections 1.2.2 and 1.2.3, we saw that the overpotential, $\eta = E - E_{eq}$, needed to deliver a current is normally a sum of separate overpotentials driving mass transfer, the electrode kinetics, and any other dynamics involved in the electrode reaction. In a reversible case all kinetics are

31 We will see in Chapter 3 that oxidation and reduction can indeed be widely separated on the potential axis, but for kinetic reasons, not for anything to do with $E^{0'}$.

32 This will not be the case for R plated onto an inert substrate in amounts less than a monolayer (e.g., the substrate electrode being Pt and R being Cu). Under those conditions, the activity of R may be considerably less than unity.

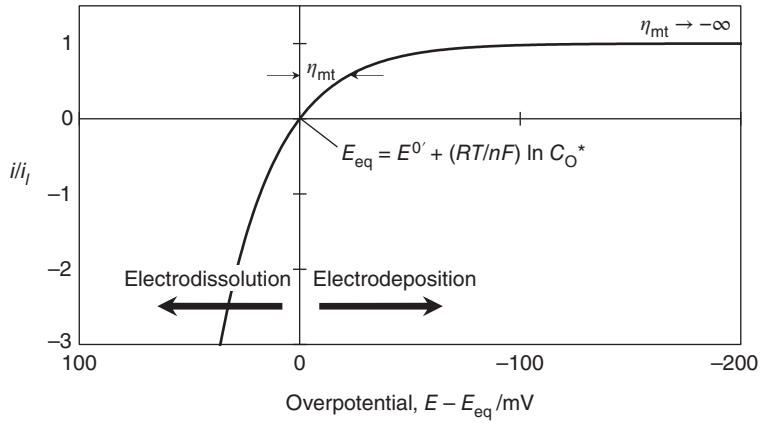



**Figure 1.3.4** Current–potential curve for a nernstian system where the reduced form is the electrode material. The potential axis is referenced to the equilibrium potential. On the negative side of $E_{eq}$, species O is reduced at the electrode and is electrodeposited on the surface. A limiting current is reached for large negative overpotentials. On the positive side of $E_{eq}$, species R is oxidized and dissolves into the solution from the surface of the electrode. Since there is no mass-transfer limitation on the availability of R at the surface, the current increases (negatively) as greater overpotentials are applied.

fast, so the overpotential is entirely a *mass-transfer overpotential*, $\eta_{mt}$.[33] Therefore,

$$\eta_{mt} = \frac{RT}{nF} \ln \left( \frac{i_l - i}{i_l} \right) \tag{1.3.25}$$

When $i = i_l$, $\eta_{mt} \to -\infty$.[34]

Equation (1.3.25) can be written in exponential form:

$$1 - \frac{i}{i_l} = \exp \left( \frac{nF\eta_{mt}}{RT} \right) \tag{1.3.26}$$

The exponential can be expanded as a power series, and the higher-order terms can be dropped if the argument is kept small; that is,

$$e^x = 1 + x + \frac{x^2}{2} + \cdots \approx 1 + x \text{ (when } x \text{ is small)} \tag{1.3.27}$$

Thus, under conditions of small deviations of potential from $E_{eq}$, the $i - \eta_{mt}$ characteristic is linear:

$$\eta_{mt} = -\frac{RTi}{nFi_l} \tag{1.3.28}$$

Since $-\eta/i$ has dimensions of resistance (ohms), we can define a "small-signal" mass-transfer resistance, $R_{mt}$, as

$$\boxed{R_{mt} = \frac{RT}{nFi_l}} \tag{1.3.29}$$

33 Sometimes called the *concentration overpotential*.

34 Since $\eta$ is a measure of polarization, this condition is sometimes called *complete mass-transfer polarization* or *complete concentration polarization*.

Here we see that the mass-transfer-limited electrode reaction resembles an actual resistance element, but only at small overpotentials.[35]

## 1.4 Semiempirical Treatment of Nernstian Reactions with Coupled Chemical Reactions

The current–potential curves discussed so far can be used to measure concentrations, mass-transfer coefficients, and stoichiometric or thermodynamic parameters, such as $n$-values and standard potentials. Under conditions where the electron-transfer rate at the interface is rate determining, they can also be employed to measure heterogeneous electron-transfer rate constants (see Chapters 3, 5, and 10). Yet another class of steady-state voltammetric behavior arises when homogeneous reactions are coupled to the electron-transfer step. In such cases, one can use electrochemical methods to find equilibrium constants and rate constants of the coupled processes.

### 1.4.1 Coupled Reversible Reactions

If a homogeneous process, fast enough to be considered always in thermodynamic equilibrium (a reversible process), is coupled to a nernstian electron-transfer reaction, then one can use a simple extension of the steady-state treatment in Section 1.3 to derive the $i-E$ curve. Consider, for example, a species O involved in an equilibrium that precedes the electron-transfer reaction[36]

$$\mathrm{A} \rightleftharpoons \mathrm{O} + q\mathrm{Y} \tag{1.4.1}$$

$$\mathrm{O} + ne \rightleftharpoons \mathrm{R} \tag{1.4.2}$$

For example, A might be an electrochemically inactive metal complex, $\mathrm{MY_q^{n+}}$; O could be the electroactive free metal ion, $\mathrm{M^{n+}}$; and Y could be a free, neutral ligand [see also Section 5.3.2(*c*)]. For reaction 1.4.2, the Nernst equation still applies at the electrode surface,

$$E = E^{0\prime} + \frac{RT}{nF} \ln \frac{C_\mathrm{O}(x=0)}{C_\mathrm{R}(x=0)} \tag{1.4.3}$$

and (1.4.1) is assumed to be at equilibrium everywhere:

$$\frac{C_\mathrm{O} C_\mathrm{Y}^\mathrm{q}}{C_\mathrm{A}} = K \qquad (\text{all } x) \tag{1.4.4}$$

hence,

$$E = E^{0\prime} + \frac{RT}{nF} \ln \left[ \frac{KC_\mathrm{A}(x=0)}{C_\mathrm{Y}^\mathrm{q}(x=0) C_\mathrm{R}(x=0)} \right] \tag{1.4.5}$$

Assuming: (a) that at $t = 0$, $C_\mathrm{A} = C_\mathrm{A}^*$, $C_\mathrm{Y} = C_\mathrm{Y}^*$, and $C_\mathrm{R} = 0$ for all $x$; (b) that $C_\mathrm{Y}^*$ is so large compared to $C_\mathrm{A}^*$ that $C_\mathrm{Y}(x=0) = C_\mathrm{Y}^*$ at all times; and (c) that $K \ll 1$, then at steady state

$$\frac{i}{nFA} = m_\mathrm{A}[C_\mathrm{A}^* - C_\mathrm{A}(x=0)] \tag{1.4.6}$$

---

35 A similar (but not identical) treatment gives $\eta_\mathrm{mt}$ and $R_\mathrm{mt}$ for any system in which an equilibrium potential is defined, e.g., when both O and R are soluble and present in the bulk, as in Section 1.3.2*(b)*. In general, $R_\mathrm{mt} = [-di/dE]^{-1}_{E=E_\mathrm{eq}}$.

36 To simplify notation, charges on all species are omitted.

$$\frac{i_l}{nFA} = m_A C_A^* \tag{1.4.7}$$

$$\frac{i}{nFA} = m_R C_R(x=0) \tag{1.4.8}$$

Then, as previously,

$$C_A(x=0) = \frac{(i_l - i)}{nFAm_A} \qquad C_R(x=0) = \frac{i}{nFAm_R} \tag{1.4.9a,b}$$

$$\boxed{E = E^{0'} + \frac{RT}{nF}\ln\frac{m_R}{m_A} + \frac{RT}{nF}\ln K - \frac{RT}{nF}q\ln C_Y^* + \frac{RT}{nF}\ln\left(\frac{i_l - i}{i}\right)} \tag{1.4.10}$$

$$E = E_{1/2} + \frac{0.059}{n}\log\frac{i_l - i}{i} \qquad (\text{at } 25^\circ\text{C}) \tag{1.4.11}$$

where

$$\boxed{E_{1/2} = E^{0'} + \frac{0.059}{n}\log\frac{m_R}{m_A} + \frac{0.059}{n}\log K - \frac{0.059}{n}q\log C_Y^*} \tag{1.4.12}$$

Thus, the $i-E$ curve, (1.4.11), has the usual nernstian shape, but $E_{1/2}$ is shifted in a negative direction (since $K \ll 1$) from the position that would be found for process 1.4.2 unperturbed by the homogeneous equilibrium. From the shift of $E_{1/2}$ with $\log C_Y^*$, both $K$ and $q$ can be determined, the latter as $-(n/0.059)(dE_{1/2}/d\log C_Y^*)$. Although these thermodynamic and stoichiometric quantities are available, no kinetic or mechanistic information can be obtained when all reactions are reversible.[37]

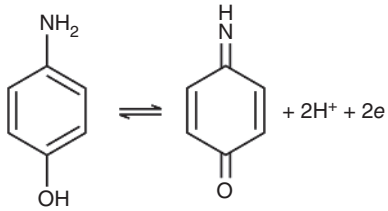
### 1.4.2 Coupled Irreversible Chemical Reactions

When an irreversible chemical reaction is coupled to a nernstian electron transfer, the $i-E$ curves can be used to provide kinetic information about the homogeneous process. Consider a nernstian charge-transfer reaction with a following first-order reaction:

$$O + ne \rightleftharpoons R \tag{1.4.13}$$

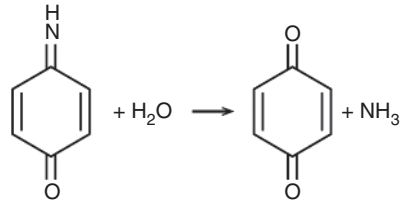
$$R \xrightarrow{k} T \tag{1.4.14}$$

where $k$ is the rate constant (in $s^{-1}$) for the further reaction of R. An example is the oxidation of *p*-aminophenol in acid solution.




(1.4.15)

37 When the mechanism was introduced above, the free metal ion was assumed to be electroactive and the complex to be electroinactive. Thinking this way simplifies a first discussion of this topic; however, the assumption is unnecessary. Since the metal ion and the complex remain in equilibrium, it is not possible to discern which species is the primary electroreactant. Mechanistic information is not available when thermodynamic equilibrium always applies.




(1.4.16)

Reaction 1.4.16 does not affect the mass transfer and reduction of O, so (1.3.7) and (1.3.10) still apply (assuming $C_O = C_O^*$ and $C_R = 0$ at all $x$ at $t = 0$). However, the reaction causes R to disappear from the electrode surface at a higher rate, and this difference affects the $i - E$ curve.

In the absence of the following reaction, we think of the concentration profile for R as decreasing linearly from a value $C_O(x = 0)$ at the surface to the point where $C_R = 0$ at $\delta$, the outer boundary of the Nernst diffusion layer. The coupled reaction adds a channel for disappearance of R, so the R profile in the presence of the reaction does not extend as far into the solution as $\delta$. Thus, the added reaction steepens the profile and augments mass transfer away from the electrode surface. For steady-state behavior, such as at a rotating disk, we assume that the rate at which R disappears from the surface to be the rate of diffusion in the absence of the reaction [$m_R C_R(x = 0)$; see (1.3.8)] plus an increment proportional to the rate of reaction [$\mu k C_R(x = 0)$]. At steady state, the rate of formation of R, given by (1.3.7), equals its total rate of disappearance; thus, we have

$$\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)] = m_R C_R(x = 0) + \mu k C_R(x = 0) \tag{1.4.17}$$

where $\mu$ is a proportionality constant having units of cm, so that the product $\mu k$ has dimensions of cm/s, as required. In the literature (3), $\mu$ is called the *reaction layer thickness*. For our purpose, it is best just to think of $\mu$ as an adjustable parameter. From (1.4.17),

$$C_O(x = 0) = \frac{i_l - i}{nFAm_O} \tag{1.4.18}$$

$$C_R(x = 0) = \frac{i}{nFA(m_R + \mu k)} \tag{1.4.19}$$

Substituting these values into the Nernst equation for (1.4.13) yields

$$\boxed{E = E^{0\prime} + \frac{RT}{nF} \ln \frac{m_R + \mu k}{m_O} + \frac{RT}{nF} \ln \left( \frac{i_l - i}{i} \right)} \tag{1.4.20}$$

or

$$E = E'_{1/2} + \frac{0.059}{n} \log \left( \frac{i_l - i}{i} \right) \qquad (\text{at } 25^\circ\text{C}) \tag{1.4.21}$$

where

$$E'_{1/2} = E^{0\prime} + \frac{0.059}{n} \log \left( \frac{m_R + \mu k}{m_O} \right) \tag{1.4.22}$$

or

$$\boxed{E'_{1/2} = E_{1/2} + \frac{0.059}{n} \log \left( 1 + \frac{\mu k}{m_R} \right)} \tag{1.4.23}$$

where $E_{1/2}$ is the half-wave potential for the kinetically unperturbed reaction.

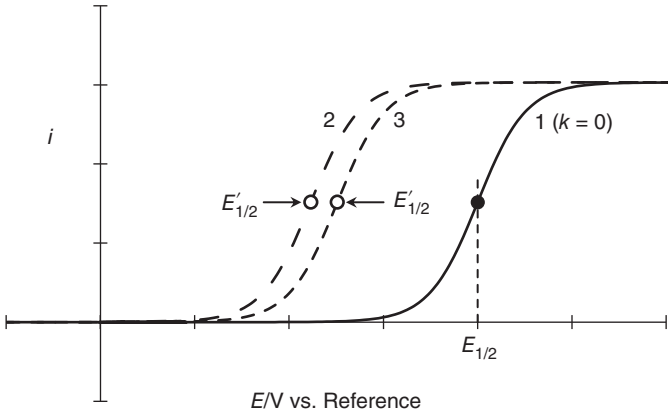



**Figure 1.4.1** Effect of an irreversible following homogeneous chemical reaction on nernstian $i-E$ curves at a rotating disk electrode. (*1*) Unperturbed curve. (*2*) and (*3*) Curves with following reaction at two rotation rates, where the rotation rate for (*3*) is greater than for (*2*).

Two limiting cases can be defined: (a) When $\mu k/m_R \ll 1$, that is $\mu k \ll m_R$, the effect of the following reaction, (1.4.14), is negligible, and the unperturbed $i-E$ curve results. (b) When $\mu k/m_R \gg 1$, the following reaction dominates the behavior and

$$E'_{1/2} = E_{1/2} + \frac{0.059}{n} \log \frac{\mu k}{m_R} \tag{1.4.24}$$

The effect is to shift the reduction wave in a *positive* direction without a change in shape. For the rotating disk electrode, where $m_R = 0.62 D_R^{2/3} \omega^{1/2} \nu^{-1/6}$, (1.4.24) becomes [assuming $\mu \neq f(\omega)$]

$$E'_{1/2} = E_{1/2} + \frac{0.059}{n} \log \frac{\mu k}{0.62 D_R^{2/3} \nu^{-1/6} \omega^{1/2}} \tag{1.4.25}$$

An increase of rotation rate, $\omega$, raises the rate of mass transfer and makes it more competitive with the following reaction. Thus, the wave shifts in a *negative* direction, toward the unperturbed wave (Figure 1.4.1). A tenfold change in $\omega$ causes a shift of $30/n$ mV.

A similar treatment can be given for other chemical reactions coupled to the electron transfer reaction (4). This approach is useful in formulating a qualitative or semiquantitative interpretation of $i-E$ curves; however, exact values of $k$ cannot be determined unless explicit expressions for $m_R$ and $\mu$ can be derived. The rigorous treatment of electrode reactions with coupled homogeneous chemical reactions is discussed in Chapter 13.

## 1.5 Cell Resistance and the Measurement of Potential

Let us now consider a cell composed of two ideally nonpolarizable electrodes, for example, two SCEs immersed in a potassium chloride solution: SCE/KCl/SCE. The $i-E$ characteristic of the ideal cell would look like that of a pure resistance (Figure 1.5.1, solid line), because the only limitation on current flow is imposed by the resistance of the solution. In fact, these conditions (i.e., paired nonpolarizable electrodes) are exactly those sought in measurements of solution conductivity. For any real electrodes (e.g., actual SCEs), mass-transfer and charge-transfer overpotentials would also become significant at high enough current densities.

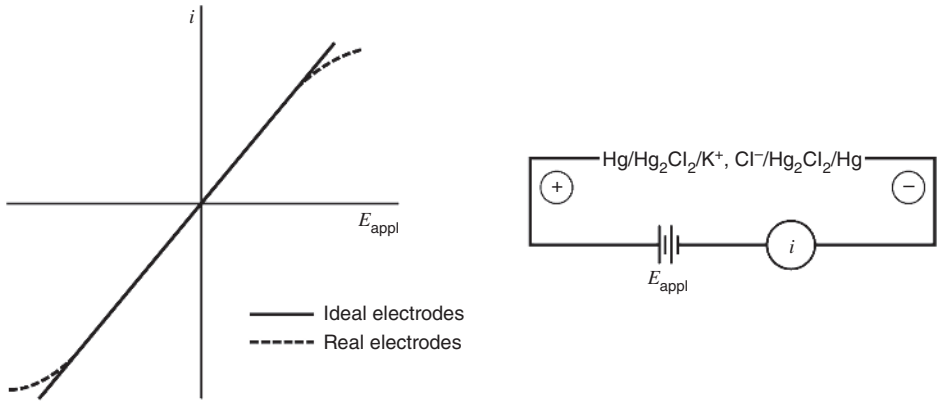



**Figure 1.5.1** Current–potential curve for a cell composed of two electrodes approaching ideal nonpolarizability. The magnitude of the slope is $1/R_s$, where $R_s$ is the solution resistance.

When the potential of any electrode is measured against a reference electrode during the passage of current, a voltage drop equal to $iR_s$ (often called the *ohmic drop*) is always included in the measured value. Here, $R_s$ is the solution resistance between the electrodes, which, unlike the impedances describing the mass transfer and activation steps in the electrode reaction, actually behaves as a true resistance over a wide range of conditions.

The inclusion of ohmic drop in measurements of potential has broad impact on electrochemical experiments, so we must begin to explore it in detail.

### 1.5.1 Components of the Applied Voltage When Current Flows

Consider once again the cell in Figure 1.2.4. At open circuit ($i = 0$), the potential of the cadmium electrode is the equilibrium value, $E_{eq,Cd}$ (about −0.64 V *vs.* SCE). We saw earlier that with $E_{appl} = -0.64$ V (Cd *vs.* SCE), no current would flow through the ammeter. If $E_{appl}$ is changed to −0.80 V (Cd *vs.* SCE), current flows. The extra applied voltage is distributed in two parts. First, to deliver the current, the potential of the Cd electrode, $E_{Cd}$, must shift to a new value, perhaps −0.70 V *vs.* SCE. The remainder of the applied voltage (−0.10 V in this example) represents the ohmic drop caused by current flow in solution. We assume that the SCE is essentially ideally nonpolarizable and does not change its potential under current flow.

In general,

$$E_{appl}(vs.\ \text{SCE}) = E_{Cd}(vs.\ \text{SCE}) - iR_s = E_{eq,Cd}(vs.\ \text{SCE}) + \eta - iR_s \tag{1.5.1}$$

in which the last two terms are related to current flow. When there is a cathodic current at the working (cadmium) electrode, both are negative. Conversely, both are positive for an anodic current. An overpotential (the total from all sources; Section 1.2.3), $\eta = E_{Cd} - E_{eq,\,Cd}$, is needed to drive the electrode reaction at the rate corresponding to the current. In the example above, $\eta = -0.06$ V. The ohmic drop, $-iR_s$, exists to deliver the net current through the electrolyte.[38]

The profile of electrostatic potential along the current path is illustrated in Figure 1.5.2, which resembles Figure 1.1.2, discussed earlier. In the prior case, the system was at open circuit, so there was no current flow. The potential inside each conducting phase was constant, and

38 The sign preceding the ohmic drop in (1.5.1) is negative because of the sign convention adopted here for currents (cathodic currents taken as positive).

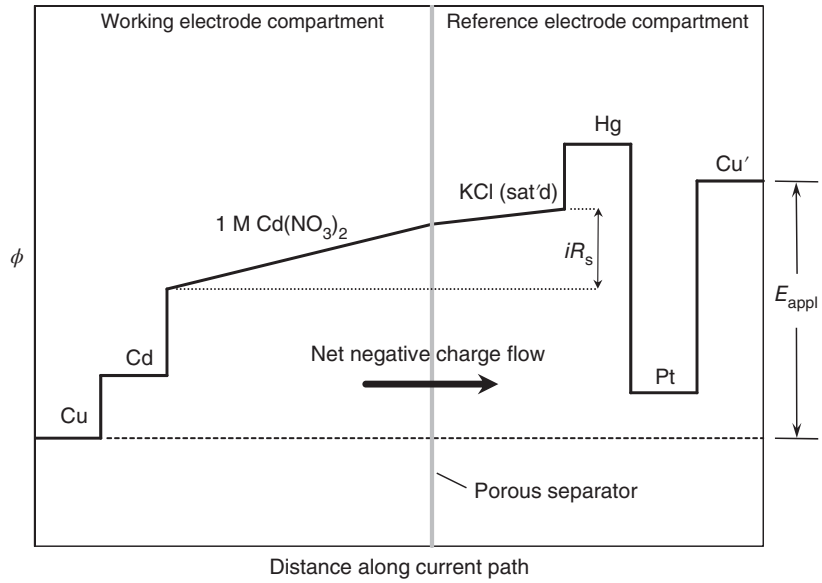



**Figure 1.5.2** Profile of electrostatic potential, $\phi$, along the current path in the cell of Figure 1.2.4. Cu and Cu′ represent the wires used to connect apparatus to the cell (as in Figure 1.1.4). The cell has two compartments, with the working electrode and the reference electrode having different electrolytes. A porous, ionically conducting separator, such as a frit, prevents mixing of the electrolytes. The slope of the potential profile differs in the two electrolytes because their conductivities are not the same.

changes in potential occurred only at the interfaces. In Figure 1.5.2, the potential inside the electrolyte phases is not constant, but slopes upward from the working electrode to the reference. This is a consequence of the current flow. The potential difference across the electrolyte (the working side *vs.* the reference side) is the ohmic drop. Inside the electrolyte, anions are driven along a sloping potential profile in the upward direction, and cations are driven in the downward direction.[39]

In this cell, different electrolytes are in contact with the working and reference electrodes. They must contact each other in a manner that permits ionic exchange (e.g., through a glass frit). This contact is called a *liquid junction* and is marked in Figure 1.5.2 with a vertical gray line. Because a liquid junction is a boundary between conducting phases, one must generally expect a discontinuity in electrostatic potential (called a *liquid junction potential*), like the stairstep at any of the other boundaries. Section 2.3 covers liquid junctions in detail, and we will see there that good design can often reduce a junction potential to a negligible level for most electrochemical work. Such is the case for Figure 1.5.2. The double slash in the corresponding cell notation in Figure 1.2.4 indicates a liquid junction that does not contribute to the overall cell potential.

In (1.5.1), the ohmic drop is separately identified from the overpotential, because it is characteristic of the bulk solution and not of the working electrode/electrolyte interface or the electrode reaction. Unfortunately, its existence in $E_{\text{appl}}$ weakens our strategy for controlling the potential at a working electrode/electrolyte interface *vs.* a reference. Our real interest is in the actual potential of the Cd electrode *vs.* the reference, i.e., $E_{\text{Cd}}$, which is corrected for $iR_{\text{s}}$.

39 Even though one sees no slope to the profile inside any of the metallic phases in Figure 1.5.2, each such segment must have an upward slope to the right, because the metals also have resistance to current flow. However, their ohmic drops are invisible on the scale of the figure, because the metals are much more conductive than the electrolytes.

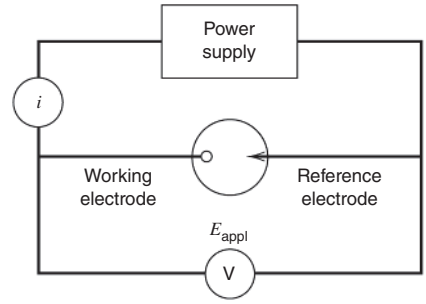



**Figure 1.5.3** Two-electrode cell.

While $E_{Cd}$ is the fundamentally important quantity, dictating the identity and rates of electrode reactions at the working electrode, $E_{appl}$ is what one can actually measure and control. In most experiments, $E_{appl}$ is the intended working electrode potential (perhaps varying in a chosen way with time), so it is generally desirable to work under conditions in which the actual working electrode potential approaches $E_{appl}$ as closely as possible, i.e., with ohmic drop minimized. Proper cell design and instrumentation are the keys to success.

### 1.5.2 Two-Electrode Cells

Under conditions where $iR_s$ is less than a few mV and the reference electrode remains unpolarized under the current flow, a *two-electrode cell* (Figure 1.5.3) can be used to determine the $i-E$ curve, just as we have been discussing. The potential of the working electrode can be taken from $E_{appl}$, either directly or with correction for the small ohmic drop. In classic experiments in aqueous solutions, two-electrode cells were often used. In these systems, it was often true that $i < 10$ μA and $R_s < 100$ Ω, so that $iR_s < 10^{-5}$ A × 100 Ω or $iR_s < 1$ mV, which is negligible for most purposes. In contemporary practice with UMEs, it has become common to employ two-electrode cells, because the currents are extremely small and $iR_s$ is typically insignificant. Figure 1.5.4*a* shows a typical two-electrode cell for work with a UME.

With larger electrodes (even in the millimeter range) or with more highly resistive solutions, such as those based on many nonaqueous solvents or with low concentrations of supporting electrolyte, serious complications can result from the ohmic drop in solution. In these situations, a three-electrode cell is used, as discussed in Section 1.5.3.[40]

### 1.5.3 Three-Electrode Cells

In experiments where $iR_s$ is too large for two-electrode cells to be effective (e.g., with high-current cells or nonaqueous electrolytes having low conductivities), a *three-electrode cell* (Figure 1.5.5) is preferable. In this arrangement, the current is passed between the working electrode and a *counter electrode*,[41] while the potential is measured against a separate reference electrode that need not carry any cell current. The counter electrode can be any convenient one, because its electrochemical properties do not affect the measurements or the behavior of the electrode of interest. It might be chosen to be an electrode that does not produce

40 This is a moment to remind the reader that the focus of this book is on electrochemical characterization methods carried out in lab-sized cells. The comments here are in keeping with that focus. Two-electrode cells are used extensively in industrial and technological situations, including synthetic cells, batteries, and fuel cells. In many of these cases, $iR_s$ is a large, sometimes dominant, part of the total voltage between the electrodes. Optimization of electrode potentials in such systems is beyond the scope of this book.

41 Or *auxiliary electrode*.

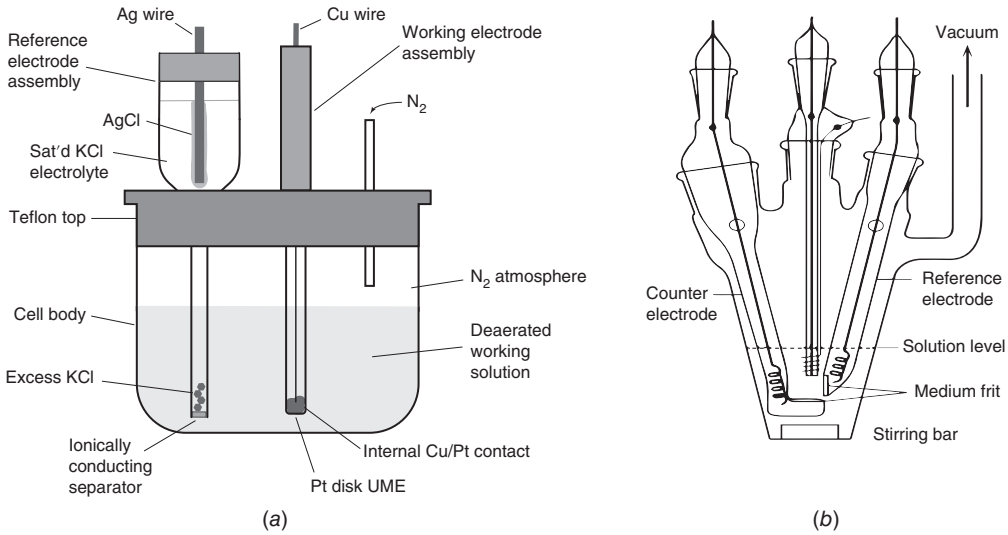



**Figure 1.5.4** Typical two- and three-electrode cells used in electrochemical experiments. (*a*) Two-electrode cell for use with a UME. The working electrode is a disk formed as the cross-section of fine Pt wire sealed in glass. $N_2$ inlet is for deaeration. Reference electrode is Ag/AgCl/KCl (sat'd). (*b*) Three-electrode cell designed for studies with nonaqueous solutions at a platinum-disk working electrode, with provision for attachment to a vacuum line for deaeration. [Part (*b*) reprinted with permission from Demortier and Bard (5). © 1973, American Chemical Society.] Three-electrode cells for bulk electrolysis are shown in Figure 12.1.1.

substances by electrolysis that will reach the working electrode surface and cause interfering reactions there. Frequently, it is placed in a compartment separated from the working electrode by an ionically conducting separator. The reference electrode is positioned with its tip near the working electrode for reasons that we will shortly discuss. An example of a three-electrode cell is shown in Figure 1.5.4*b*.

The device used to measure the potential difference between the working electrode and the reference electrode has a high input impedance, so that a negligible current is drawn through the reference electrode. Consequently, its potential will remain constant and equal to its open-circuit value.

In a three-electrode cell, $E_{appl}$ is the voltage of the working electrode *vs.* the reference, just as in two-electrode cells, and remains the measured/controlled quantity in most experiments.

This three-electrode arrangement is widely used for electrochemical experiments. An instrument that manifests the electrical capabilities in Figure 1.5.5 is called a *potentiostat* (Section 1.9.1 and Chapter 16).

### 1.5.4 Uncompensated Resistance

In the three-electrode arrangement, the $iR_s$ term is partly—sometimes even largely—removed from the measured potential of the working electrode. However, it is not entirely removed. Consider the potential profile in solution between the working and counter electrodes, shown schematically in Figure 1.5.6. (The profile in an actual cell depends on the electrode shapes, geometry, solution conductance, etc.) The solution between the electrodes can be regarded as a potentiometer (often a highly nonlinear one). If the reference electrode is placed anywhere but exactly at the electrode surface, some fraction of $iR_s$, (denoted as $iR_u$, where $R_u$ is the *uncompensated resistance*) will be included in the measured potential. The good news is that the larger part of $iR_s$ has been removed from the measured potential (i.e., has been "compensated") by

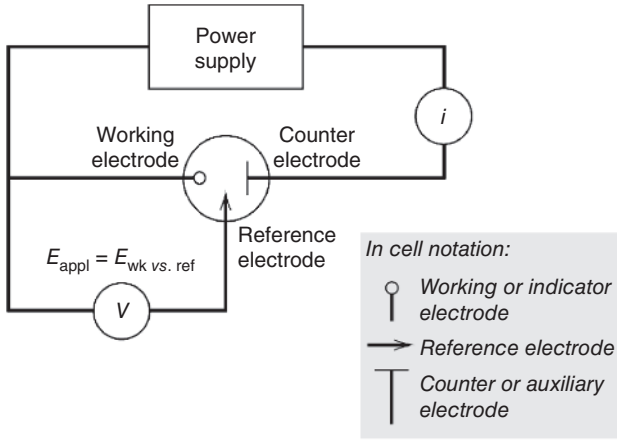



**Figure 1.5.5** Three-electrode cell and notation for the different electrodes.

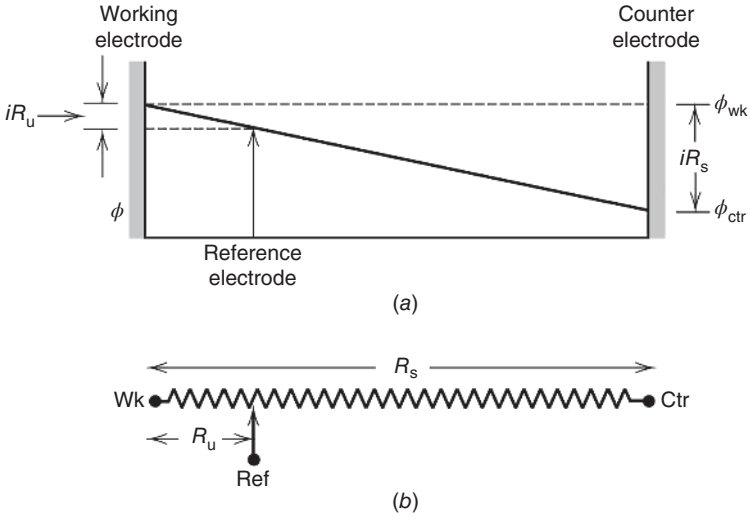



**Figure 1.5.6** (*a*) Potential drop between working and counter electrodes in solution and $iR_u$ measured at the reference electrode. (*b*) Representation of the cell as a potentiometer.

employing the three-electrode configuration. The *compensated resistance* is denoted in this book as $R_c$, so that $R_u + R_c = R_s$.

Even when the reference electrode is designed for very close placement to the working electrode by use of a fine tip called a *Luggin–Haber capillary*, some uncompensated resistance remains. The uncompensated potential drop can sometimes be removed separately, e.g., from steady-state measurements by measurement of $R_u$ and point-by-point correction of each value of potential. Electrochemical instrumentation frequently includes provisions for electronic compensation of $iR_u$ (Chapter 16).

One can think of a three-electrode cell as comprising two distinct cells, a *reference cell* and a *current-carrying cell*, having the working electrode in common. Figure 1.5.7 shows the potential profiles through both component cells of a system in which the working electrode is $Cd/Cd^{2+}$(5 mM), $KNO_3$ (1 M) and the reference electrode is an SCE (as in Figures 1.2.4 and 1.5.2), while the counter electrode is Pt in 1 M $HNO_3$. The reference cell is therefore

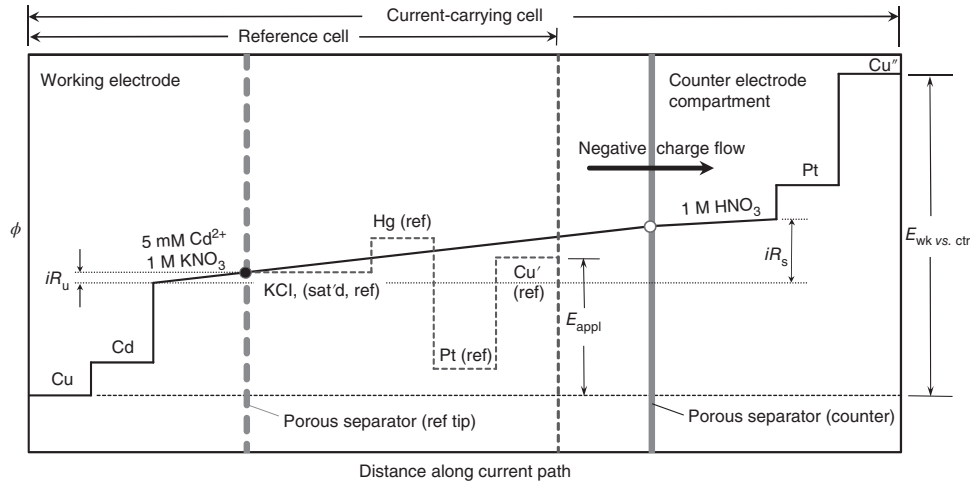



**Figure 1.5.7** Potential profiles across a three-electrode cell. Solid profile describes the current-carrying cell (working and counter electrodes). Dashed gray lines show components of the reference electrode. Working and reference electrodes make up the reference cell. At the black circle on the left, the reference electrode tip makes connection to the potential profile in the current-carrying cell. The liquid junction between working and counter electrode compartments is at the porous separator on the right. Cu, Cu′, and Cu″ are copper wires contacting the working, reference, and counter electrodes, respectively.

$Cu/Cd/Cd^{2+}(5\ mM)$, $KNO_3$ (1 M)//KCl (sat'd)/$Hg_2Cl_2$/Hg/Pt/Cu′, and the current-carrying cell is $Cu/Cd/Cd^{2+}(5\ mM)$, $KNO_3$ (1 M)//$HNO_3$ (1 M)/Pt/Cu″. The liquid junction between the tip of the reference electrode and the working solution is close to the working electrode, as shown in Figure 1.5.7.

The potential profile in the electrolyte inside the reference electrode is flat, because there is only a tiny current flow through the reference electrode; however, the reference cell still includes part of the overall ohmic drop in the current-carrying cell ($-iR_u$), because the reference and current-carrying cells share the solution segment between the working electrode and the reference cell's contact point.

The potential profiles in the electrolytes of the current-carrying cell slope upward to the right, because current moves along the whole path. The total ohmic drop across this cell is $-iR_s$, several times larger than $-iR_u$.

The measured potential of the working electrode would be determined *vs.* the SCE (as $E_{appl}$), and the actual potential, $E$, would be given by correction for the uncompensated ohmic drop:

$$\boxed{E = E_{appl} + iR_u} \tag{1.5.2}$$

This equation is also valid for a two-electrode system. In that case, the full solution resistance across the cell is uncompensated; thus, $R_c = 0$ and $R_u = R_s$.

If the reference capillary has a tip diameter $d$, it can be placed as close as $2d$ from the working electrode surface without causing appreciable shielding error, where *shielding* denotes a partial blockage of the current path in solution, modifying the current densities at the working electrode surface.

For a planar electrode with uniform current density across its surface,

$$R_u = x/\kappa A \tag{1.5.3}$$

where $x$ is the distance of the capillary tip from the electrode, $A$ is the electrode area, and $\kappa$ is the solution conductivity.

The effect of $iR_u$ can be particularly serious for spherical microelectrodes, such as the hanging mercury drop electrode or the dropping mercury electrode (DME), because most of the resistive drop occurs close to the electrode. For a spherical electrode of radius $r_0$,

$$R_u = \frac{1}{4\pi\kappa r_0}\left(\frac{x}{x + r_0}\right) \tag{1.5.4}$$

For a reference electrode tip placed just one electrode radius away ($x = r_0$), $R_u$ is already half of the value for the tip placed infinitely far away.

Any resistance in the working electrode itself (e.g., in thin wires used to make ultramicroelectrodes, in semiconductor electrodes, or in resistive films on the electrode surface) will also appear in $R_u$.

In this section, we have come to see how uncompensated ohmic drop is included in the measured or controlled potential of the working electrode; however, there is more to the story. In the next section, we will see that $R_u$ is also a determining factor in the time response of an electrochemical cell.

## 1.6 The Electrode/Solution Interface and Charging Current

### 1.6.1 The Ideally Polarizable Electrode

No charge transfer can occur across the metal/solution interface at an IPE (Section 1.2.2), regardless of the potential imposed by an outside source of voltage. While no real electrode can behave as an IPE over the whole available potential range, some electrode/solution systems can approach ideal polarizability over limited ranges. For example, a mercury electrode in contact with a deaerated potassium chloride/potassium hydroxide solution approaches the behavior of an IPE in a window about 2 V wide. At sufficiently positive potentials, the mercury can oxidize:

$$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e \qquad (\text{near} + 0.25\ \text{V}\ \textit{vs.}\ \text{NHE}) \tag{1.6.1}$$

and at very negative potentials $K^+$ can be reduced:

$$K^+ + e \xrightarrow{Hg} K(Hg) \qquad (\text{near} - 2.1\ \text{V}\ \textit{vs.}\ \text{NHE}) \tag{1.6.2}$$

These are the electrode reactions that define the background limits in this system. In the potential range between these processes, charge-transfer reactions are not significant. Even though the reduction of water,

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \tag{1.6.3}$$

is thermodynamically possible over much of that range, it occurs at a very low rate at a mercury surface, unless quite negative potentials are applied. The only faradaic current flowing in this region is due to charge-transfer reactions of trace impurities (e.g., metal ions, oxygen, and organic species), and this current is quite small in clean systems. Another electrode that behaves as an IPE is a gold surface hosting an adsorbed self-assembled monolayer of alkane thiol (Section 17.1).

### 1.6.2 Capacitance and Charge at an Electrode

Since charge cannot cross the IPE interface when the potential is changed, the behavior of the electrode/solution interface is analogous to that of a capacitor, an electrical circuit element

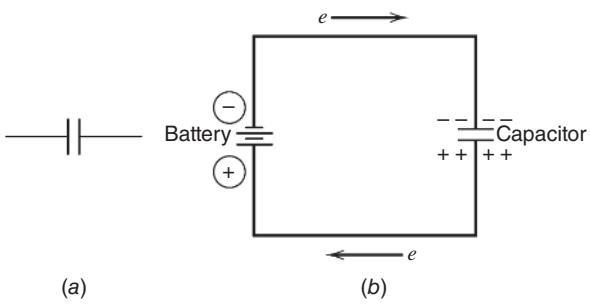



**Figure 1.6.1** (*a*) A capacitor. The gap between the plates could be a vacuum or could be filled with a gaseous, liquid, or solid insulator. (*b*) Charging a capacitor with a battery.

composed of two metal sheets separated by a dielectric (an insulating material; Figure 1.6.1*a*). Its behavior is governed by

$$\frac{q}{E} = C \tag{1.6.4}$$

where $q$ is the charge stored on the capacitor (in coulombs, C), $E$ is the potential difference across the capacitor (in volts, V), and $C$ is the capacitance (in farads, F). When $E$ is applied, charge will accumulate on the metal plates of the capacitor until $q$ satisfies (1.6.4). For example, if a 2-V battery is placed across a 10-μF capacitor, current will flow until 20 μC has accumulated. The charge consists of an excess of electrons on one plate and a deficiency of electrons on the other (Figure 1.6.1*b*). During this process, a transient current (called a *charging current*) flows in the external circuit connecting the two plates. Its magnitude depends on the resistance in the circuit (Section 1.6.4).

The electrode/solution interface has been shown experimentally to behave like a capacitor, and a model of the interfacial region somewhat resembling a capacitor can be given. At any potential, there will exist a charge on the electrode, $q^{\mathrm{M}}$, and a charge in the solution, $q^{\mathrm{S}}$ (Figure 1.6.2). Whether the charge on the electrode is negative or positive with respect to the solution depends on the potential across the interface and the composition of the solution. At all times, however, $q^{\mathrm{M}} = -q^{\mathrm{S}}$ (Section 2.2.2).[42] The charge on the electrode, $q^{\mathrm{M}}$, represents an excess or deficiency of electrons and resides in a very thin layer at the electrode surface (<1 nm in the case of a metal electrode). The charge in solution, $q^{\mathrm{S}}$, is made up of an excess of either cations or anions in the vicinity of the electrode surface. The charges $q^{\mathrm{M}}$ and $q^{\mathrm{S}}$ are often divided by the electrode area, $A$, and expressed as *charge densities*, e.g., $\sigma^{\mathrm{M}} = q^{\mathrm{M}}/A$, usually given in μC/cm$^2$. The whole array of charged species and oriented dipoles existing at the electrode/solution interface is called the *electrical double layer* (although its structure may be more complex than two charged layers, as we will see next).

At a given potential, the electrode/solution interface is characterized by a *double-layer capacitance*, $C_{\mathrm{d}}$, typically in the range of 10–40 μF/cm$^2$. However, unlike real capacitors, whose capacitances are independent of the voltage across them, an electrochemical double layer typically has a $C_{\mathrm{d}}$ that depends on potential.[43]

### 1.6.3 Brief Description of the Electrical Double Layer

The solution side of the double layer is itself understood to comprise layers. That closest to the electrode, the *inner layer*, contains solvent molecules and sometimes other species (ions

42 In an actual experimental arrangement, two electrodes and two interfaces, would have to be considered; however, we concentrate our attention here on one interface and ignore what happens at the other.

43 In various equations in the literature and in this book, $C_{\mathrm{d}}$ may express the capacitance per unit area and be given in μF/cm$^2$, or it may express the capacitance of a whole interface and be given in μF. The usage for a given situation is always apparent from the context or from a dimensional analysis.

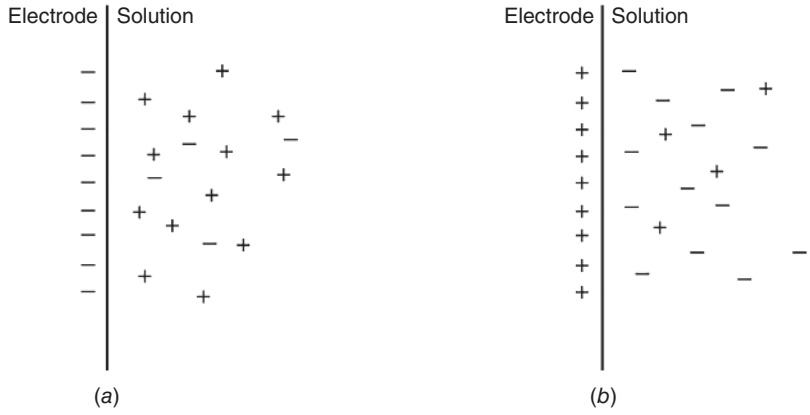



**Figure 1.6.2** The electrode/solution interface as a capacitor with a charge on the electrode, $q^M$, (*a*) negative and (*b*) positive.

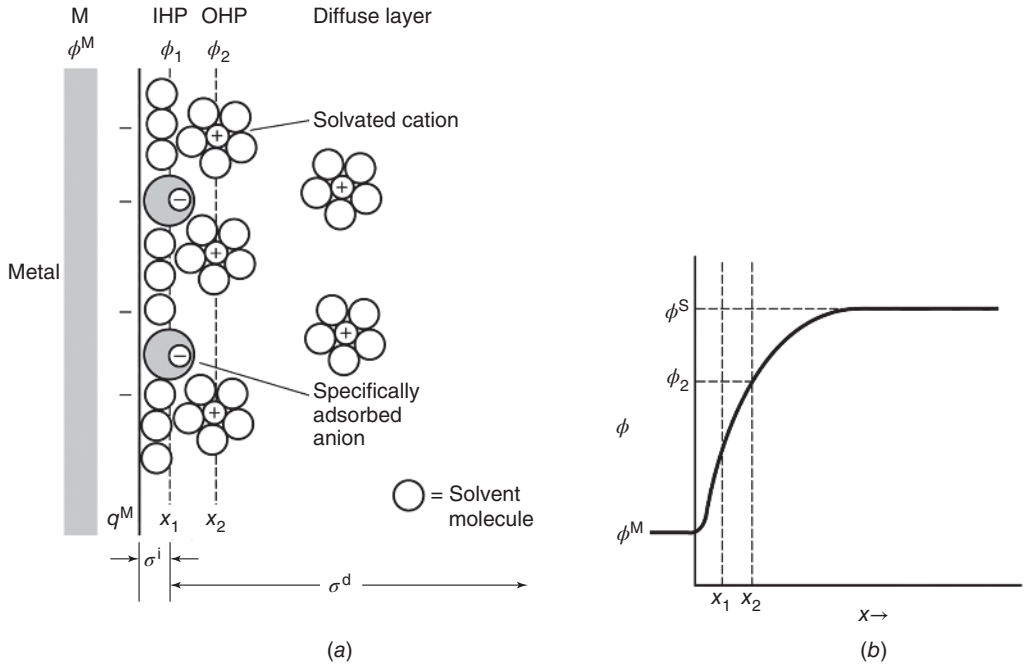



**Figure 1.6.3** (*a*) A model of the double-layer region under conditions where anions are specifically adsorbed. (*b*) Potential profile across the double-layer region in the absence of specific adsorption of ions. The *electric potential, ϕ*, is discussed in detail in Section 2.2. A more quantitative representation of this profile is shown in Figure 14.3.6.

or molecules) that are said to be *specifically adsorbed* (Figure 1.6.3*a*). This inner layer is also called the *compact*, *Helmholtz*, or *Stern layer*. The locus of the electrical centers of specifically adsorbed ions), at a distance $x_1$, is called the *inner Helmholtz plane* (IHP). The total charge density in this inner layer is $\sigma^i$ ($\mu C/cm^2$). Solvated ions cannot approach the metal as closely as $x_1$, but only to $x_2$, called the *outer Helmholtz plane* (OHP). The interaction of the solvated ions with the charged metal involves only long-range electrostatic forces, which are essentially

independent of the chemical properties of the ions. These ions are said to be *nonspecifically adsorbed*. Because of thermal agitation (i.e., Brownian motion), the nonspecifically adsorbed ions are distributed in a three-dimensional region called the *diffuse layer*, which extends from the OHP into the bulk of the solution.[44] The excess charge density in the diffuse layer is $\sigma^{d}$; hence, the total excess charge density on the solution side of the double layer, $\sigma^{S}$, is given by

$$\boxed{\sigma^{S} = \sigma^{i} + \sigma^{d} = -\sigma^{M}} \tag{1.6.5}$$

The thickness of the diffuse layer depends on the total ionic concentration in the solution. For concentrations greater than $10^{-2}$ M, it is less than ~10 nm. The potential profile across the double-layer region is shown in Figure 1.6.3*b*. Adsorption and double-layer structure are considered in much greater detail in Chapter 14.

The structure of the double layer can affect the rates of faradaic processes (Section 14.7). Consider an electroactive species that is not specifically adsorbed. This species can approach the electrode only to the OHP, and the potential it experiences there, $\phi_2$, differs from the potential in bulk solution, $\phi^{S}$, by the potential drop across the diffuse layer, $\phi_2 - \phi^{S}$. For example, $\phi_2 - \phi^{S}$ in 0.1 M NaF is −0.021 V at $E = -0.55$ V *vs.* SCE, but is somewhat larger in magnitude at more negative and more positive potentials. One can often neglect double-layer effects in considering electrode reactions, but at other times they must be taken into account.[45,46]

One usually cannot neglect the existence of the double-layer capacitance or the presence of a charging current in electrochemical experiments. Indeed, we will see in the next section that double-layer charging is central to the establishment of potential differences in cells and to the control of potential.

### 1.6.4 Double-Layer Capacitance and Charging Current

Consider a two-electrode cell consisting of an IPE paired with a reference electrode that can pass modest currents without significant change of composition or potential. We can approximate such a system with a mercury electrode in a KCl solution contacted by an SCE. This cell, $Hg/K^{+}$, $Cl^{-}$/SCE, can be modeled by an electrical circuit with a resistor, $R_s$, representing the solution resistance and a capacitor, $C_d$, representing the double layer at the $Hg/K^{+}$, $Cl^{-}$ interface (Figure 1.6.4).[47,48]

Information about an electrochemical system is often gained by applying an electrical perturbation and observing the response. In later chapters, we will encounter such experiments in

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44 *Nonspecific adsorption* is a well-established term in the literature, but it can lead to confusion. Actually, nonspecifically adsorbed ions are not adsorbed at all within the meaning usually attached to the idea of adsorption, which involves chemical binding of an adsorbate to a surface. In electrochemistry, nonspecifically adsorbed ions are said to be "adsorbed" because they are in excess in the interfacial region.

45 In the example just given, the potential at the OHP is −21 mV *vs.* bulk solution; thus, each electronic state on a molecule or ion at the OHP is 21 meV higher in energy than for the same species in bulk solution. This makes the species at the OHP a little easier to oxidize or a little harder to reduce. That 21 meV is about equal to $kT$ (the Boltzmann constant times absolute temperature, 25.7 meV at 25°C), so it is big enough to produce noticeable kinetic effects in situations where precise rate constants are meaningful, but it is not so big as to be of concern when only the magnitude of kinetic data is being sought.

46 Double-layer structure can even affect the thermodynamics of a redox couple if the members of the couple are confined to the electrode surface, as in the case of an electroactive adsorbate.

47 Actually, the capacitance of the SCE, $C_{SCE}$, must also be included. The total series capacitance of $C_d$ and $C_{SCE}$ is $C_T = C_d C_{SCE}/(C_d + C_{SCE})$. Normally the SCE would be designed to have a much larger area, so that $C_{SCE} \gg C_d$ and $C_T \approx C_d$. Thus, $C_{SCE}$ can be neglected in the circuit.

48 Since $C_d$ at a real electrode is generally a function of potential, the proposed model in terms of circuit elements is strictly accurate only for experiments where the overall cell potential does not change very much. Where it does, approximate results can be obtained using an average $C_d$ over the potential range.

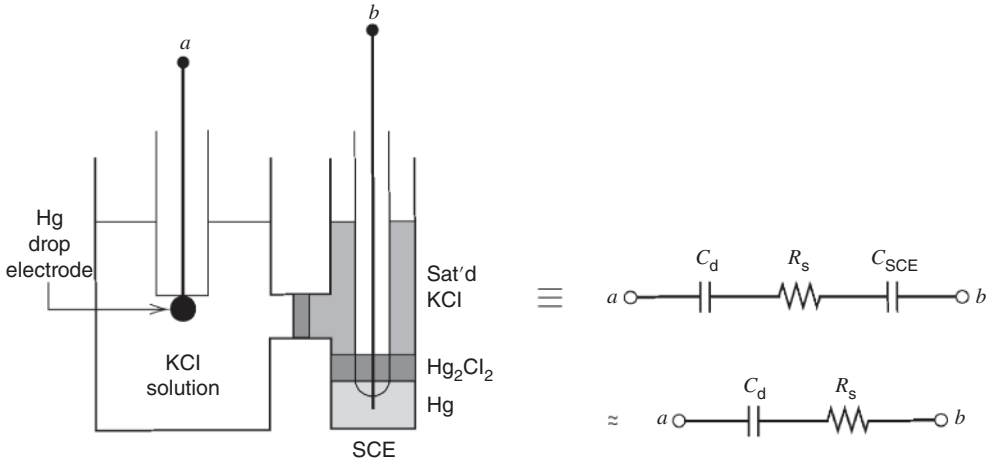



**Figure 1.6.4** *Left*: Two-electrode cell with an ideally polarizable mercury drop electrode and an SCE. *Right*: Representation of the cell in terms of linear circuit elements.

many forms. It is worthwhile now to consider the response of an IPE to two common electrical perturbations: the potential step and the potential sweep.[49]

***(a) Potential (or Voltage) Step***

The treatment of a voltage step at the IPE is the familiar RC-circuit problem (Figure 1.6.5). Suppose the network of $R_s$ and $C_d$ initially has no voltage across it, so that the capacitor is uncharged and there is no current through the resistor. The behavior of the current, $i$, with time, $t$, when applying a step of magnitude $E$, is

$$i = \frac{E}{R_s} e^{-t/R_s C_d} \tag{1.6.6}$$

This equation is derived from (1.6.4), which can be written in terms of the voltage across the double-layer capacitor, $E_C$ as

$$q = C_d E_C \tag{1.6.7}$$

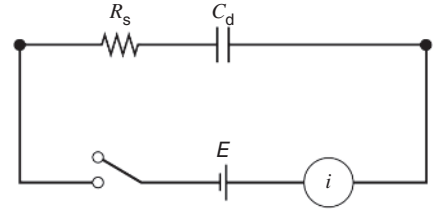
At $t > 0$, the sum of the voltages, $E_R$ and $E_C$, across the resistor and the capacitor, respectively, must equal the applied step; hence,

$$E = E_R + E_C = iR_s + \frac{q}{C_d} \tag{1.6.8}$$

Recognizing that $i = dq/dt$, we obtain, with rearrangement,

$$\frac{dq}{dt} = \frac{-q}{R_s C_d} + \frac{E}{R_s} \tag{1.6.9}$$

**Figure 1.6.5** Potential step experiment for an RC circuit.




49 The first and second editions also cover the case in which a constant current is applied.

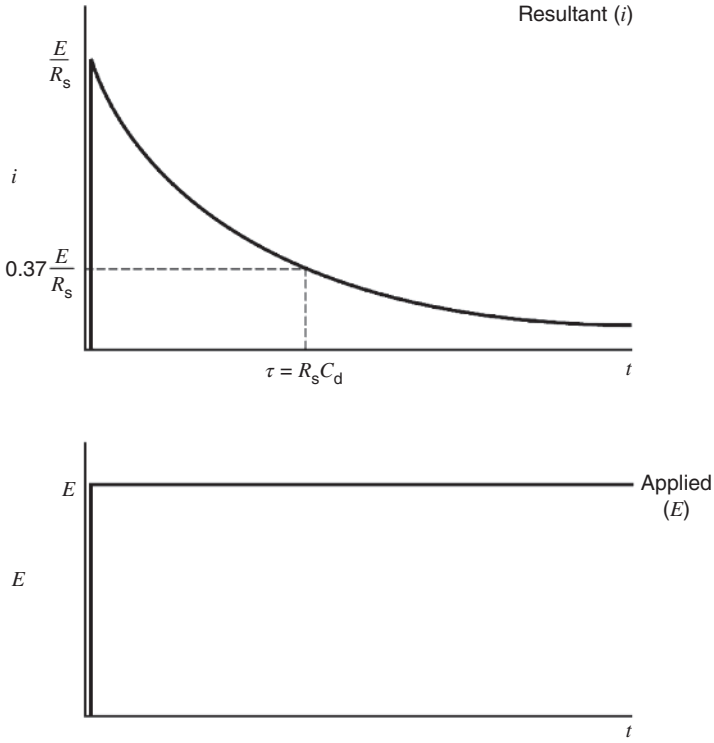



**Figure 1.6.6** Current transient (*i vs.* *t*) resulting from a potential step experiment.

The solution of (1.6.9) is

$$q = EC_d[1 - e^{-t/R_sC_d}] \tag{1.6.10}$$

By differentiating (1.6.10), one obtains (1.6.6).

Thus, a potential step produces an exponentially decaying charging current having a *time constant*, $\tau = R_sC_d$ (Figure 1.6.6). The current drops to 37% of its initial value at $t = \tau$, and to 5% of its initial value at $t = 3\tau$. If $R_s = 1\ \Omega$ and $C_d = 20\ \mu F$, for example, then $\tau = 20\ \mu s$ and double-layer charging is 95% complete in 60 μs.

The treatment for a real electrochemical cell is somewhat more complicated, because the working electrode's potential, $E$, is defined arbitrarily by the choice of the reference electrode. Applying a zero voltage across the cell or a zero potential *vs.* the reference electrode does not mean that the working electrode becomes uncharged.[50] That happens when the working electrode is at $E_z$, the *potential of zero charge* (PZC), which is defined by the nature of the electrode and solution. The voltage across $C_d$ at any moment is $E - E_z$, and the charge on the electrode is[51]

$$q = C_d(E - E_z) \tag{1.6.11}$$

Also, we dealt in the treatment above only with the magnitude of the step and did not worry about its direction or about the sign of the current. We will fix these points in the following treatment.

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50 A corollary is that the potential drop across the working electrode/electrolyte interface is generally not zero when a zero potential *vs.* the reference electrode is applied.

51 This $q$ is the same as $q^M$ above. Charge is frequently discussed from the perspective of the working electrode and symbolized without the superscript.

Now suppose that we have a three-electrode cell, as in Section 1.5.3. A potentiostat continuously measures and controls $E_{appl}$, the voltage applied at the working electrode *vs.* the reference electrode (perhaps an SCE). At $t = 0$, $E_{appl}$ is abruptly changed from one value, $E_1$, to another, $E_2$. We assume that the double layer at the working electrode is fully charged before the step, so that no current flows through the solution. Accordingly, there is no ohmic drop in the solution, and the potential of the working electrode is also $E_1$. After $t = 0$, when $E_{appl}$ becomes $E_2$, the potential of the working electrode is driven to change in the same direction. The charge on $C_d$ must change, too, and a current must flow through the solution resistance. From (1.5.2), the potential of the working electrode at any moment is,

$$E = E_2 + iR_u \tag{1.6.12}$$

where $R_u$ is the uncompensated resistance (Section 1.5.4).[52] Now, let us subtract $E_z$ from both sides, then multiply by $C_d$.

$$C_d(E - E_z) = C_d(E_2 - E_z) + iR_uC_d \tag{1.6.13}$$

From (1.6.11), we recognize the left side as $q$, the charge on the working electrode at any moment, and we see that the first term on the right is $q_2$, the double-layer charge on the working electrode when its potential arrives at the step potential, $E_2$. Also, we know that $i = -dq/dt$ (given the current convention), so by substitution and rearrangement we obtain

$$\frac{dq}{dt} = -\frac{q}{R_uC_d} + \frac{q_2}{R_uC_d} \tag{1.6.14}$$

which has the same form as (1.6.9). The solution is, however, not a form of (1.6.10), because we cannot assume the double layer at the working electrode to be uncharged at $t = 0$. Indeed, we have already assumed that it was equilibrated at $E_1$ before the step, so the initial charge on the double layer would be

$$q_1 = C_d(E_1 - E_z) \tag{1.6.15}$$

In Problem A.9, the reader can show that the solution to (1.6.14) with that initial condition is

$$q = q_2 - (q_2 - q_1)e^{-t/R_uC_d} = q_2 - C_d\Delta Ee^{-t/R_uC_d} \tag{1.6.16}$$

where we have recognized $q_2 - q_1$ as $C_d\Delta E$, with $\Delta E = E_2 - E_1$.

The charging current is then derived from (1.6.16) as $-dq/dt$.[53]

$$\boxed{i = -\frac{\Delta E}{R_u}e^{-t/R_uC_d}} \tag{1.6.17}$$

By substitution into (1.6.12), we find the potential of the working electrode to be

$$\boxed{E = E_2 - \Delta Ee^{-t/R_uC_d}} \tag{1.6.18}$$

Figure 1.6.7 shows behavior typical of a hanging Hg drop in 0.1 M KCl *vs.* an SCE (i.e., in a three-electrode version of the cell in Figure 1.6.4). There are three noteworthy points:

1) Any change of potential at an electrode is inseparable from a concomitant charging of the double layer at that electrode. Indeed, interfacial charging is the means by which the potential of a conducting phase is established, as we will see in greater detail in Chapter 2.
2) The potential at the working electrode does not immediately follow $E_{appl}$. It takes time to charge the double layer at the working electrode—at least several times $R_uC_d$.

52 Equation (1.6.12) is general for both two-electrode and three-electrode cells. In the former case, $R_u = R_s$.

53 This can be viewed as the same result as in (1.6.6). For that case, $R_u = R_s$, and $\Delta E = E$.

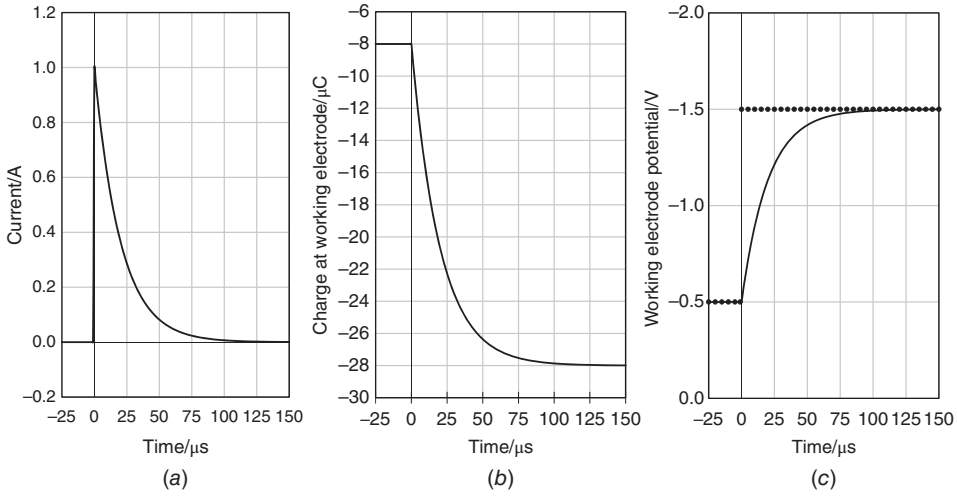


**Figure 1.6.7** Behavior at a mercury working electrode to which a voltage step is applied. Before $t = 0$, $E_{appl} = -0.5$ V, after which it is stepped to −1.5 V. $R_u = 1\ \Omega$, $C_d = 20\ \mu F$, $E_z = -0.1$ V, cell time constant = 20 μs. (*a*) Current. (*b*) Double-layer charge on the working electrode: $q_1 = -8\ \mu C$ and $q_2 = -28\ \mu C$. (*c*) $E$ (solid curve) and $E_{appl}$ (points) *vs*. the reference.

3) The current passed in the charging process decays exponentially after the step is applied, but it can be quite large at first. In the system relating to Figure 1.6.7, the initial charging current is 1 A, and the voltage drop across the uncompensated resistance at $t = 0$ is 1 V, the entirety of the applied step. These are big effects.

***(b) Linear Potential Sweep (or Voltage Ramp)***

In many electrochemical experiments, one desires that $E_{appl}$ start at some initial value, $E_1$, then change linearly with time at a sweep rate (or scan rate), $\nu$ (in V/s), until a final value, $E_2$, is reached (Figure 1.6.8*a*).[54]

$$E_{appl} = E_1 - \nu t \tag{1.6.19}$$

We assume that the double layer at the working electrode is fully charged at $E_1$ before the sweep starts, so that there is no current flow through the solution, and the potential of the working electrode is $E_1$. At $t = 0$, the sweep begins. Because the potential at the working electrode is continuously changing, the charge on the double layer must be continuously altered, too. A charging current must flow through the cell, and it will produce a voltage drop in solution. The potential of the working electrode is

$$E = E_1 - \nu t + iR_u \tag{1.6.20}$$

The same procedures used to transform (1.6.12) into (1.6.14) allow (1.6.20) to become

$$\frac{dq}{dt} = -\frac{q}{R_u C_d} + \frac{q_1}{R_u C_d} - \frac{\nu t}{R_u} \tag{1.6.21}$$

where $q_1$ is the initial charge on the double layer at the working electrode, given by (1.6.15).

54 In this book and most of the literature, the scan rate, $\nu$, is an absolute quantity, having no sign. Scan direction is reflected by explicit signs in equations. Equation (1.6.19) describes a negative-going scan.

The solution to this differential equation is

$$q = q_1 - \nu t C_d + \nu R_u C_d^2 (1 - e^{-t/R_u C_d}) \tag{1.6.22}$$

and the current is found as $-dq/dt$, or

$$\boxed{i = \pm \nu C_d \left(1 - e^{-t/R_u C_d}\right)} \qquad (+ \text{ for neg. scan}, - \text{ for pos. scan}) \tag{1.6.23}$$

The development through (1.6.22) is for a negative-going scan and would lead to a positive sign before $\nu$ in (1.6.23). For a positive-going scan, the signs before $\nu$ would be reversed in (1.6.20)–(1.6.22). The final result is given explicitly for both directions in (1.6.23).

For a negative-going scan, the current increases from zero after the scan starts. Over several cell time constants, it attains a steady value, $\nu C_d$ (Figure 1.6.8*b*), which can be used to estimate $C_d$.

Alternatively, one can let $E_{appl}$ follow a *triangular wave* (i.e., a voltage ramp whose sweep direction reverses at some potential, $E_\lambda$, as in Figure 1.6.9*a*). For the case of a negative-going forward scan, the triangular wave is expressed as

$$E_{appl} = E_1 - \nu t \qquad 0 \le t \le |E_\lambda - E_1|/\nu \tag{1.6.24}$$

$$E_{appl} = E_\lambda + \nu t \qquad t > |E_\lambda - E_1|/\nu \tag{1.6.25}$$

The steady-state current changes from $\nu C_d$ during the forward scan to $-\nu C_d$ during the reverse scan. The result for a system with constant $C_d$ is shown in Figure 1.6.9 for the case of a negative-going initial scan.

#### *(c) Charging Current in Electrochemical Measurements*

We have taken care with charging current here, because a great fraction of electrochemical experimentation involves it. Most strategies are based on changes, over time, of potential, interfacial structure, or even electrode area; consequently, a charging current generally exists

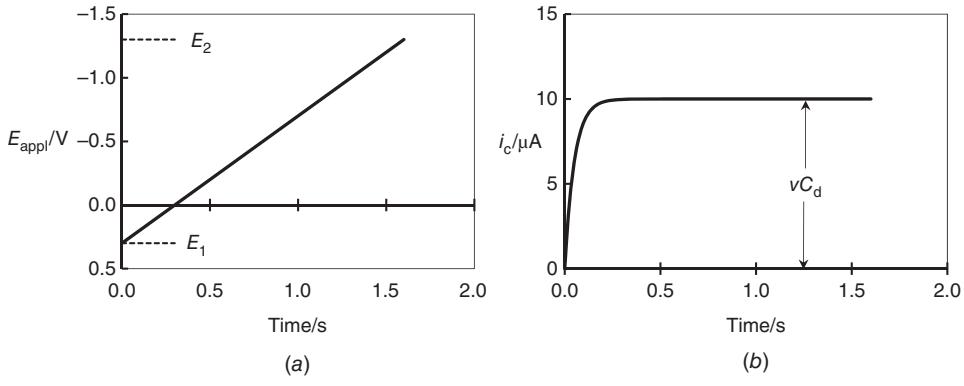


**Figure 1.6.8** Behavior resulting from a linear potential sweep applied to a working electrode at which only double-layer charging can occur. (*a*) $E_{appl}$ *vs.* time (working *vs.* reference). (*b*) Charging current *vs.* time. $R_u = 5$ kΩ, $C_d = 10$ μF, $R_u C_d = 50$ ms, $E_1 = 0.3$ V, $E_2 = -1.3$ V, $\nu = 1$ V/s.

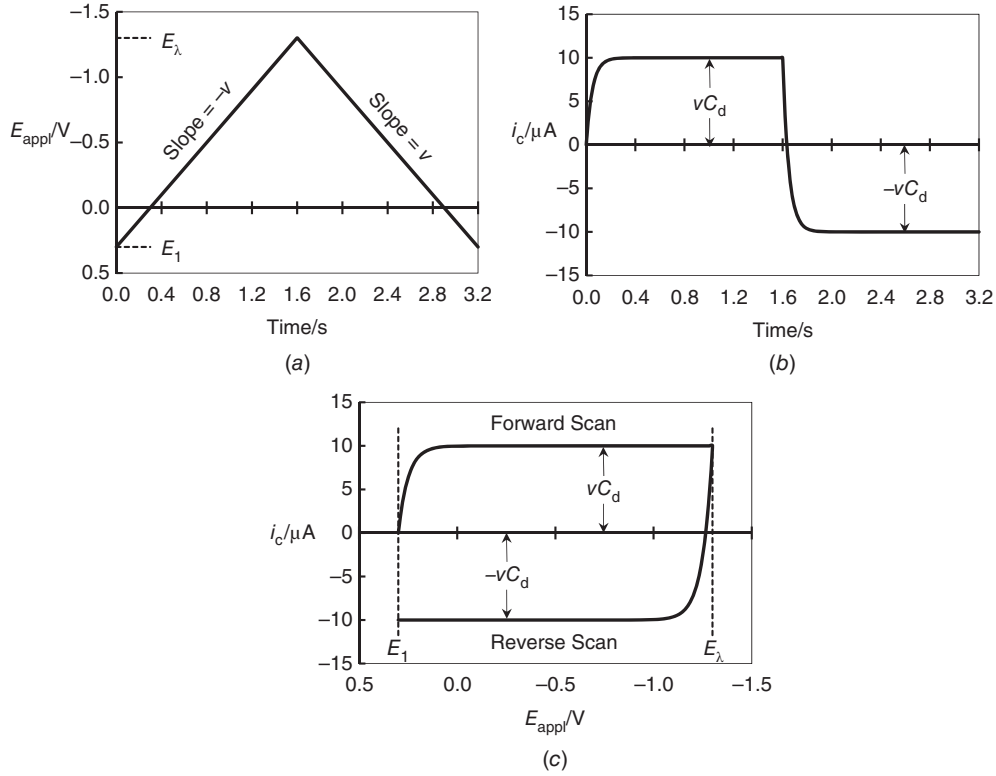


**Figure 1.6.9** Behavior resulting from a cyclic linear potential sweep applied to a working electrode at which only double-layer charging can occur. (*a*) $E_{appl}$ *vs*. time (working *vs*. reference). (*b*) Charging current *vs*. time. (*c*) Charging current *vs*. $E_{appl}$. Cell parameters are as for Figure 1.6.8. $E_1 = 0.3$ V, $E_\lambda = -1.3$ V, $v = 1$ V/s.

and contributes to a background against which faradaic currents are observed.[55] The charging current frequently interferes with measurements of faradaic currents. When the electroactive species are present at low concentrations (e.g., as in trace analysis), the charging current can be much larger than any faradaic current of interest and commonly defines detection limits. In later chapters, we will return repeatedly to this issue and to strategies for dealing with it.

Still, one must not regard charging current as simply a background concern. It is integral to the control of potential in electrochemical systems, so it is essential to experimental design and execution. Moreover, it provides access to the surface charge on the electrode and to the interfacial capacitance, which are informative about interfacial structure. In some work, the charging current is the main concern, providing access to the information sought about a system.

#### *(d) A Last Word about $E_{appl}$*

In Sections 1.5 and 1.6, we have focused on the distinction between the potential of the working electrode, $E$, and the voltage applied externally to the working electrode, $E_{appl}$, *vs*. the reference. These two quantities differ by the uncompensated ohmic drop, $iR_u$.

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55 The idea of a background current was introduced in Section 1.1.7(*b*). In most experiments, it is the sum of a charging current plus faradaic currents from the solvent, supporting electrolyte, electrode material, or impurities. Near the background limits, faradaic currents from primary components of the system predominate, but between the background limits, there may be a region where the background current is mainly charging current.

In most electrochemical experiments, one desires to control the potential of the working electrode, and $E_{appl}$ is the vehicle of control. At every moment, it is the target for $E$. If $E_{appl}$ is programmed as a step or a sweep, for example, one desires that the working electrode follow faithfully enough for theoretical treatments of the experiment to be valid. We have seen that $E$ does not follow $E_{appl}$ strictly. How well it follows depends on the cell time constant and the magnitude of the uncompensated ohmic drop, so one must be attentive to these matters.

Fortunately, it is often practical to establish experimental conditions under which $E$ does follow $E_{appl}$ well enough. This will be true when

- The cell time constant can be made short compared to the time scale[56] of the experiment.
- The uncompensated ohmic drop is small.

Both of these conditions can usually be satisfied if the solution is sufficiently conductive and the working electrode area is small enough. Depending on the system, it may be necessary to use a three-electrode cell and employ electronic compensation of resistance (Section 16.7.3).

Because $E$ is practically the same as $E_{appl}$ in most experimental work, experienced practitioners rarely distinguish these quantities as they speak and write. They simply say, for example, that they have taken $E$ (rather than $E_{appl}$) through a step program or a triangular wave. They depict the step or the sweep ideally, even though they well understand the nonideality at a step edge or at the turning point of a sweep. In published figures, such as voltammograms, they will show the potential axis as $E$, even though the instruments that produce the figures actually use $E_{appl}$.

In the rest of this book, we will follow the same practice. Further reference will rarely be made to $E_{appl}$. Unless a cautionary point is being made, we will just assume that we can control $E$ ideally enough, even as we take it through complex programs. We will just have to remain on the lookout for effects of uncompensated ohmic drop in recorded results.

## 1.7 Organization of this Book

This book has been structured to support options for teachers and students as they follow their own paths into the subject. Figure 1.7.1 illustrates possibilities.

The left column comprehends the essential core, presented in the first seven chapters. It is best to cover this material in sequence, because core ideas and treatments are generally constructed on preceding concepts.

In the right column, the teacher and student gain extensive flexibility to tailor further study according to interests and available time. The dots by the individual chapters and the dashed arrows signal that the chapters are, for the most part, independently selectable after prior study through Chapter 7. Even though the book is built as a complete story, with all chapters designed to be addressed in sequence (signified by the solid arrows), a reader can be effective by covering a few chapters in the right column.

The final group also allows for selective study; however, Chapters 17–21 are generally built on knowledge from the Advanced Fundamentals group (Chapters 13–16).

There are also appendices providing support for students as they work through this text. The mathematical techniques in Appendix A are extensively employed in Chapters 5–13. It will ease

56 The *time scale* of an experiment is an important concept that we will encounter repeatedly. It refers generally to the time period over which the most important data are recorded. For example, it might be taken as the duration of measurements after a potential step or the time required to sweep across a voltammetric wave. If the working electrode potential is to accurately follow time variations in $E_{appl}$, the cell time constant must be significantly shorter than the experimental time scale.

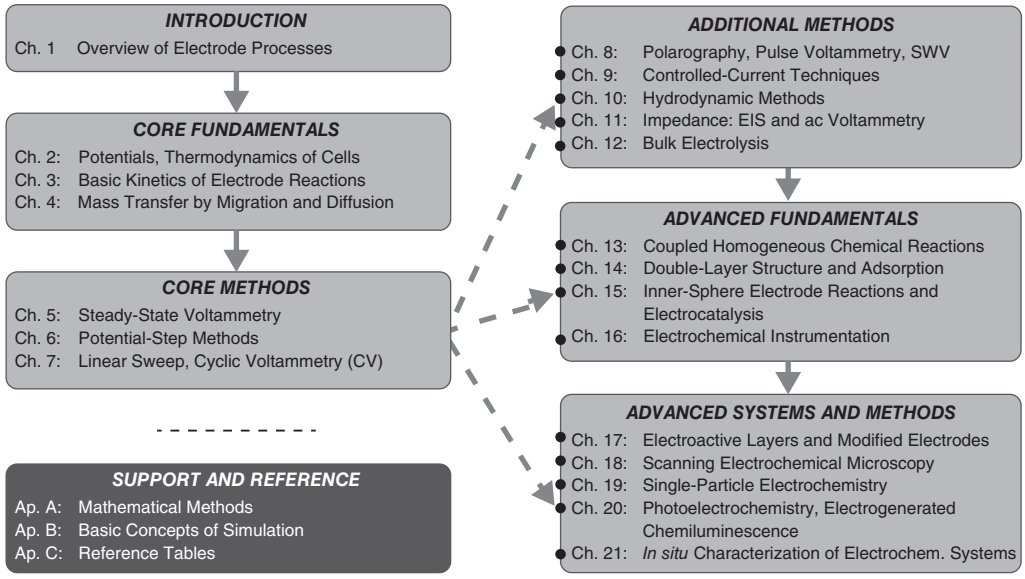


**Figure 1.7.1** Major groups of chapters.

the reader's progress to have worked through, or at least to have reviewed, Appendix A before starting Chapter 5. Appendix B is an introduction to digital simulation methods, which are widely used to address complex problems of contemporary interest. The need for simulation will come up throughout the book, beginning in Chapter 5. Appendix C is a set of reference tables useful for the end-of-chapter problems and for daily activity.

## 1.8 The Literature of Electrochemistry

Under this heading in the second edition, there was an extensive summary of the English-language literature of electrochemistry as it existed in 2001. Prominent books and monographs were listed in several categories. Review series and key journals were identified. The present reader might find that summary useful, even now.

In this edition, an equivalent summary is not provided. Mainly, the authors desire to save the space for other matters, but also relevant is that publication patterns have changed greatly since 2001, especially for articles on original research. A summary is, in many respects, no longer practical.

However, it seems still worthwhile to list general reference sources (including compilations of data), sources on laboratory techniques, and the main review series, which give rise to many references in this text.

### 1.8.1 Reference Sources

1) Bard, A. J., G. Inzelt, and F. Scholz, Eds., "Electrochemical Dictionary," 2nd ed., Springer, Heidelberg, 2012.
2) Bard, A. J., and H. Lund, Eds., "Encyclopedia of the Electrochemistry of the Elements" (18 volumes), Marcel Dekker, New York, 1973–1986.

3) Bard, A. J., R. Parsons, and J. Jordan, Eds., "Standard Potentials in Aqueous Solutions," Marcel Dekker, New York, 1985.
4) Conway, B. E., "Electrochemical Data," Elsevier, Amsterdam, 1952.
5) Horvath, A. L., "Handbook of Aqueous Electrolyte Solutions: Physical Properties, Estimation, and Correlation Methods," Ellis Horwood, Chichester, UK, 1985.
6) Janz, G. J., and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook" (2 volumes), Academic, New York, 1972.
7) Meites, L., and P. Zuman, "Electrochemical Data," Wiley, New York, 1974.
8) Meites, L., and P. Zuman et al., "CRC Handbook Series in Organic Electrochemistry" (6 volumes), CRC, Boca Raton, FL, 1977–1983.
9) Meites, L., and P. Zuman et al., "CRC Handbook Series in Inorganic Electrochemistry" (8 volumes), CRC, Boca Raton, FL, 1980–1988.
10) Parsons, R., "Handbook of Electrochemical Data," Butterworths, London, 1959.
11) Zemaitis, J. F., D. M. Clark, M. Rafal, and N. C. Scrivner, "Handbook of Aqueous Electrolyte Thermodynamics: Theory and Applications," Design Institute for Physical Property Data (for the American Institute of Chemical Engineers), New York, 1986.
12) Zoski, C. G., Ed., "Handbook of Electrochemistry," Elsevier, Amsterdam, 2007.

### 1.8.2 Sources on Laboratory Techniques

In this book, general and specialized sources on electrochemical phenomena and theory are cited in subsequent chapters; however, books on laboratory techniques generally are not. The following list is offered now as an aid to the reader:

1) Adams, R. N., "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, 1969.
2) Gileadi, E., E. Kirowa-Eisner, and J. Penciner, "Interfacial Electrochemistry—An Experimental Approach," Addison-Wesley, Reading, MA, 1975.
3) Kissinger, P. T., and W. R. Heineman, Eds., "Laboratory Techniques in Electroanalytical Chemistry," 2nd ed., Marcel Dekker, New York, 1996.
4) Sawyer, D. T., A. Sobkowiak, and J. L. Roberts, Jr., "Electrochemistry for Chemists," 2nd ed., Wiley, New York, 1995.
5) Scholz, F., Ed., "Electroanalytical Methods," 2nd ed., Springer, Berlin, 2010.
6) Zoski, C. G., Ed., "Handbook of Electrochemistry," Elsevier, Amsterdam, 2007.

### 1.8.3 Review Series

A number of review series dealing with electrochemistry and related areas exist. Volumes are published from time to time and contain chapters written by authorities.[57, 58]

1) "Advances in Electrochemical Science and Engineering" (18 volumes), H. Gerischer, C. W. Tobias, R. C. Alkire, D. M. Kolb, J. Lipkowski, P. N. Ross, L. A. Kibler, P. N. Bartlett, and M. T. Koper, Eds., Wiley-VCH, Weinheim, Germany, 1990–2018.

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57 Most of these series have had long lives and evolving editorships and publishers. They are cited below with all editors who have ever been engaged, in order of appearance, and with the publisher of the most recent volume. Individual volumes may have involved a subset of the listed editors or a different publisher.

58 Articles in the series numbered 1, 2, 4, and 7 are cited in this book, and often elsewhere in the literature, in journal reference format with the abbreviations *Adv. Electrochem. Sci. Engr.*, *Adv. Electrochem. Electrochem. Engr.*, *Electroanal. Chem.,* and *Mod. Asp. Electrochem.*, respectively. Series 4 should not be confused with *J. Electroanal. Chem.*

2) "Advances in Electrochemistry and Electrochemical Engineering" (13 volumes), P. Delahay, C. W. Tobias, and H. Gerischer, Wiley, New York, 1961–1984.
3) "Comprehensive Treatise of Electrochemistry" (10 volumes), E. Yeager, J. O'M. Bockris, B. E. Conway, S. Sarangapani, R. E. White, S. Srinivasan, and Yu. A. Chizmadzhev, Eds., Plenum, New York, 1984.
4) "Electroanalytical Chemistry" (27 volumes), A. J. Bard, I. Rubinstein, and C. G. Zoski, Eds., Taylor and Francis, Boca Raton, FL, 1966–2017.
5) "Electrochemistry (Specialist Periodical Reports)" (10 volumes), G. J. Hills (Vols. 1–3), H. R. Thirsk (Vols. 4–7), and D. Pletcher (Vols. 8–10), Senior Reporters, The Chemical Society, London, 1971–1985.
6) "Encyclopedia of Electrochemistry" (11 volumes), A. J. Bard and M. Stratmann, Series Eds., Wiley-VCH, Wenheim, Germany, 2002–2007.
7) "Modern Aspects of Electrochemistry" (60 volumes), J. O'M. Bockris, B. E. Conway, R. E. White, C. G. Vayenas, Series Eds., Springer, New York, 1954–2022.
8) "Techniques of Electrochemistry" (3 volumes), E. Yeager and A. J. Salkind, Eds., Wiley-Interscience, New York, 1972–1978.

## 1.9 Lab Note: Potentiostats and Cell Behavior

This note is intended to help the reader to gain practical familiarity with a basic electrochemical instrument, with electrical responses of cells, and with some instrumental limitations.

### 1.9.1 Potentiostats

To carry out the suggested work, you will need access to a potentiostat – the central tool in most electrochemical laboratories. This is a device for controlling a three-electrode cell and for providing information about its behavior. The potentiostat essentially manifests the functions surrounding the cell in Figure 1.5.5. It normally connects to the working, reference, and counter electrodes through a cable with clip leads.[59]

A potentiostat uses feedback circuitry to automatically control the power delivered between the working and counter electrodes, so that $E_{appl}$, the voltage applied at the working electrode *vs*. the reference, remains continuously equal to a programmed value, even if that value changes with time (see also Figure 5.1.1 and related discussion). The voltage across the current-carrying path (working electrode to counter electrode) and the current in that path are functions of $E_{appl}$ and its time dependence. Within practical limits, the potentiostat will deliver whatever is needed to fulfill the control condition. Common potentiostats can place ±13–14 V across the cell and can furnish a current of ±100 mA. "Powerful" instruments can deliver ±100 V and ±1 A. Chapter 16 provides extensive discussion of these systems.

As discussed in Section 1.6.4(*d*), $E_{appl}$ is a continuous target for the actual working electrode potential, $E$, *vs*. the reference. One generally selects conditions such that $E$ tracks $E_{appl}$ faithfully enough for valid application of theory.

Normally, one desires that $E_{appl}$ (and, therefore, also $E$) be taken through a *waveform* (such as a step or cyclic sweep). This is achieved by varying inputs of the potentiostat with time according to the desired waveform. Chapter 16 covers the details.

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59 A potentiostat can also be used with a two-electrode cell. In that case, the leads for both the counter and reference electrodes are connected to the reference.

Many modern potentiostats, including practically all routine instruments now found in electrochemical laboratories, are fully integrated and automated. Computers oversee all operations, including management of the cell, waveform generation, data recording, and presentation of results. You should use an instrument of this kind for the experiments suggested below.

### 1.9.2 Background Processes in Actual Cells

In our zeal to investigate the properties of a particular species, we sometimes neglect thorough study of the properties of the blank electrolyte (the identical solution with the species of interest omitted). This is usually just the solvent and supporting electrolyte, e.g., deaerated aqueous 1 M KCl or buffer solution. As described in Sections 1.1.7(*b*) and 1.6.4(*c*), the current measured in this blank electrolyte solution informs the experimenter of the anodic and cathodic potential limits and the magnitude of the charging current. This measurement is also critically important in identifying unexpected faradaic currents resulting from impurities in the supporting electrolyte and solvent. If not identified (and eliminated, if possible), these currents may be mistaken for signatures of the redox process of interest, leading to erroneous conclusions.

One can study background processes for many different electrode/electrolyte combinations. A simple experiment is to use an inexpensive commercial glassy carbon (GC) disk electrode with a diameter of 1–3 mm as the working electrode. The GC electrode should be placed into a deaerated 0.1 M KCl solution together with a Pt counter electrode and a commercial Ag/AgCl reference electrode. Deaeration is easily achieved by bubbling the solution with nitrogen for a few minutes and then maintaining a nitrogen atmosphere over the solution in the cell. The counter electrode should have an area significantly larger than that of the working electrode. Typically, Pt foil or mesh is used, but commercial Pt counter electrodes are also readily available. For homemade Pt counter electrodes, it is important to make sure that any non-Pt electrical connections to the electrode are not exposed to the solution, as these may readily oxidize and contaminate the solution (e.g., Cu wire oxidation).

After constructing the cell and connecting the potentiostat leads, perform a cyclic voltammetric experiment in the blank electrolyte by scanning the potential at 0.1 V/s over a potential range where the electrode behaves nearly as an IPE. A safe range is between −0.5 and 0.5 V *vs*. Ag/AgCl. Plot the cyclic voltammogram and determine the value of $C_d$ for the GC electrode/0.1 M KCl interface from the steady-state charging current. Do not expect your voltammograms in blank solutions to be as ideal looking as Figure 1.6.9*c*; most common electrode/electrolyte interfaces do not behave as an IPE over large potential ranges. Explore how far positive and negative the GC electrode potential can be scanned before significant currents arise, marking the potential window for the system.

Carry out a potential step experiment to determine $R_u$ and $C_d$ in your blank solution, but be sure to keep $E$ in the IPE-like zone. Plot ln $i$ *vs*. $t$, where $t$ is measured from the step edge. Your instrument might be able to make this plot for you, but if not, just export the data and make the plot yourself with a spreadsheet. You should be able to obtain the cell time constant from the slope and $R_u$ from the intercept. From these measurements, estimate how fast one can charge the GC/0.1 M KCl interface. Investigate the effects of order-of-magnitude changes of electrolyte concentration on $R_u$ and $C_d$. If you have additional working electrodes of much different area, consider using them to study the effect of area on $R_u$ and $C_d$.

While the above experiments may appear elementary, they are important for evaluating the available potential range over which useful electrochemical measurements can be made, as well as the time constant of the cell under study. Experienced electrochemists will always make these background measurements when beginning to study a new system to ensure that background

processes and cell properties do not interfere with or limit the intended measurement with the species of interest.

### 1.9.3 Further Work with Simple RC Networks

To explore a wider range of time scales, you can investigate the responses of resistor-capacitor networks connected to the potentiostat in place of a real cell. The network in Figure 1.9.1 mimics an IPE, because the working electrode exhibits only the double-layer capacitance, $C_d$. The solution resistance is divided into compensated and uncompensated values, $R_c$ and $R_u$, as discussed in Section 1.5.4.

RC networks that are built as substitutes for real cells are typically called *dummy cells*. The three-element dummy cell in Figure 1.9.1 provides a good model for double-layer charging and is useful both as a teaching tool and for testing the transient characteristics of potentiostats.

Construct a network like that in Figure 1.9.1 using an electronics breadboard to readily connect the two resistors and a capacitor in series. A useful first set of components is $C_d = 10$ μF, $R_u = 1$ kΩ, $R_c = 10$ kΩ. This combination gives a cell time constant of 10 ms, so transient double-layer charging should take place in less than 50 ms. The leads from the potentiostat should be connected to the circuit as noted in the diagram.

Using the automated user interface for the potentiostat, set the instrument to perform a potential step experiment from $E_1 = -0.5$ V to $E_2 = -1.5$ V.[60] Use a step duration of $10R_uC_d$. As in the case with the real cell, plot ln $i$ *vs.* $t$ (with $t$ measured from the step edge) and obtain the cell time constant from the slope and $R_u$ from the intercept. Test the agreement between your experimental values of $R_u$ and $C_d$ against those used to construct the dummy cell.

Investigate the effects of varying $E_1$, $\Delta E = E_2 - E_1$, $R_c$, $R_u$, and $C_d$, including changes over orders of magnitude for the latter three parameters. When using smaller values for $R_u$ and $C_d$, you may find that the ln $i$ *vs.* $t$ plot becomes nonlinear at very short times due to the internal filters and output limitations of the potentiostat that you are using. Estimate the time required for the potentiostat to establish $E_{appl}$ between the working and reference electrodes.

Perform a cyclic voltammetry (triangular wave) experiment between +0.5 and −0.5 V on the original three-element network to see if the response resembles that in Figure 1.6.9*c*. Using the steady-state charging current, determine the value of $C_d$ and see how closely it matches the value of the capacitor in your circuit. Next, vary the scan rate over at least an order of magnitude and observe the dependence of the charging current on $v$. You should observe that the steady-state charging current increases linearly with scan rate. This behavior is generally seen in real electrochemical systems.

Electrochemical research groups often find dummy cells helpful for testing experimental equipment and arrangements. A common application is to calibrate the $i/E$ response of the potentiostat and to check for nonzero instrumentation offsets in either $E$ or $i$.

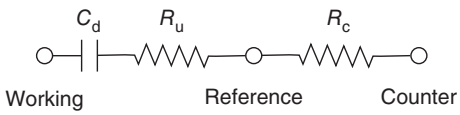


**Figure 1.9.1** A three-element network responding much like an IPE. Connection points for the potentiostat leads are noted.

60 The instrument might be set up only to perform double-step experiments, such as $E_1$ to $E_2$, then back to $E_1$. You can use this mode. Just ignore the data for the second step.

## 1.10 References


1 L. R. Faulkner, *J. Chem. Educ.*, **60**, 262 (1983).
2 L. R. Faulkner in "Physical Methods in Modern Chemical Analysis," Vol. 3, T. Kuwana, Ed., Academic, New York, 1983, pp. 137–248.
3 P. Delahay, "New Instrumental Methods in Electrochemistry," Wiley-Interscience, New York, 1954, p. 92.
4 See, for example, G. J. Hoytink, J. Van Schooten, E. de Boer, and W. Aalbersberg, *Rec. Trav. Chim.*, **73**, 355 (1954), for an application to the study of reactions coupled to the reduction of aromatic hydrocarbons.
5 A. Demortier and A. J. Bard, *J. Am. Chem. Soc.*, **95**, 3495 (1973).


## 1.11 Problems

**1.1** Consider each of the following electrode/solution interfaces. Write the equations for the electrode reactions that occur when the potential is moved progressively (1) negatively and (2) positively from the open-circuit potential, until the background limit is reached. Next to each reaction write the approximate potential for the reaction in V *vs.* SCE (assuming the reaction is reversible). Sketch the entire $i-E$ curve for the system.

a) Pt/$Cu^{2+}$(0.01 M), $Cd^{2+}$(0.01 M), $H_2SO_4$(1 M)
b) Pt/$Sn^{2+}$(0.01 M), $Sn^{4+}$(0.01 M), HCl(1 M)
c) Hg/$Cd^{2+}$(0.01 M), $Zn^{2+}$(0.01 M), HCl(1 M)

**1.2** A rotating disk electrode of area 0.30 $cm^2$ is used for the reduction of 0.010 M $Fe^{3+}$ to $Fe^{2+}$ in 1 M $H_2SO_4$. Given $D_O$ for $Fe^{3+}$ at $5.2\times10^{-6}$ $cm^2/s$, $\nu = 0.010$ $cm^2/s$, and the expression for $m_O$ in footnote 29, calculate the limiting current for the reduction for a disk rotation rate of 10 r/s. Include units on variables during calculation and give units of current in the answer.

**1.3** A solution of volume 50 $cm^3$ contains $2.0\times10^{-3}$ M $Fe^{3+}$ and $1.0\times10^{-3}$ M $Sn^{4+}$ in 1 M HCl. This solution is examined by voltammetry at a rotating platinum disk electrode of area 0.30 $cm^2$. At the rotation rate employed, both $Fe^{3+}$ and $Sn^{4+}$ have mass-transfer coefficients, $m$, of $10^{-2}$ cm/s. (a) Calculate the limiting current for the reduction of $Fe^{3+}$ under these conditions. (b) A current–potential scan is taken from +1.3 to −0.40 V *vs.* NHE. Make a labeled, quantitatively correct, sketch of the $i-E$ curve that would be obtained. Assume that no changes in the bulk concentrations of $Fe^{3+}$ and $Sn^{4+}$ occur during this scan and that all electrode reactions are nernstian.

**1.4** The conductivity of a 0.1 M KCl solution is 0.013 $\Omega^{-1}$ $cm^{-1}$ at 25 °C. (a) Calculate the solution resistance between two parallel planar platinum electrodes of 0.1 $cm^2$ area placed 3 cm apart in this solution. (b) A reference electrode with a Luggin capillary is placed the following distances from a planar platinum working electrode ($A = 0.1$ $cm^2$) in 0.1 M KCl: 0.05, 0.1, 0.5, 1.0 cm. What is $R_u$ in each case? (c) Repeat the calculations in part (b) for a spherical working electrode of the same area. [In (b) and (c), assume that a large counter electrode is employed.]

**1.5** A 0.1-$cm^2$ electrode with $C_d = 20\ \mu F/cm^2$ is subjected to a potential step under conditions where $R_u$ is 1, 10, or 100 Ω. In each case, what is the cell time constant, and what is the time required for the double-layer charging to be 95% complete?

**1.6** Suppose the potential step in Problem 1.5 is from $E_1 = -0.1$ V to $E_2 = -0.6$ V *vs.* Ag/AgCl and the PZC is −0.3 V *vs.* Ag/AgCl. (a) Calculate the charge on the working electrode at $E_1$ and $E_2$. Do the same for a PZC at (b) +0.1 V and (c) −0.1 V *vs.* SCE.

**1.7** For the electrode in Problem 1.5, what nonfaradaic current will flow (neglecting any transients) when the electrode is subjected to linear sweeps at 0.02, 1, 20 V/s?

**1.8** Consider the nernstian half-reaction:

$$A^{3+} + 2e \rightleftharpoons A^{+} \qquad E^{0'}_{A^{3+}/A^{+}} = -0.500\ \text{V } vs.\text{NHE}$$

The *i*–*E* curve for a solution at 25 °C containing 2.00 mM $A^{3+}$ and 1.00 mM $A^{+}$ in excess electrolyte shows $i_{l,c} = 4.00\ \mu A$ and $i_{l,a} = -2.40\ \mu A$. (a) What is $E_{1/2}$ (V *vs.* NHE)? (b) Sketch the expected $i - E$ curve for this system. (c) Sketch the "log plot" (analogous to Figure 1.3.2*b*) for the system.

**1.9** Consider the system in Problem 1.8 under the conditions that a complexing agent, $L^-$, which reacts with $A^{3+}$ according to the reaction

$$A^{3+} + 4L^- \rightleftharpoons AL_4^- \qquad K = 10^{16}$$

is added to the system. For a solution at 25 °C containing only 2.0 mM $A^{3+}$ and 0.1 M $L^-$ in excess inert electrolyte, answer parts (a), (b), and (c) in Problem 1.8. (Assume $m_O$ is the same for $A^{3+}$ and $AL_4^-$)

**1.10** Derive the current–potential relationship under the conditions of Section 1.3.2 for a system where R is initially present at a concentration $C_R^*$ and $C_O^* = 0$. Consider both O and R soluble. Sketch the expected $i - E$ curve.

**1.11** Suppose a mercury pool of 1 $cm^2$ area is immersed in a 0.1 M sodium perchlorate solution. How much charge (order of magnitude) would be required to change its potential by 1 mV? How would this be affected by a change in the electrolyte concentration to $10^{-2}$ M? Why?

**1.12** Rearrangement of equation (1.3.17) yields the following expression for *i* as a function of *E*, which is convenient for calculating $i - E$ curves for nernstian reactions:

$$i/i_l = \{1 + \exp[(nF/RT)(E - E_{1/2})]\}^{-1} \tag{1.11.1}$$

a) Derive this expression.
b) Consider the half-reaction $Ru(NH_3)_6^{3+} + e \rightleftharpoons Ru(NH_3)_6^{2+}$. The $E^0$ for this reaction is given in Appendix C. A steady-state $i - E$ curve is obtained with a solution containing 10 mM $Ru(NH_3)_6^{3+}$ and 1 M KCl (as supporting electrolyte). The working electrode is a Pt disk of area 0.10 $cm^2$ operating under conditions where $m = 10^{-3}$ cm/s for both Ru species. Use a spreadsheet to calculate and plot the expected $i - E$ curve.

**1.13** a) Derive an expression for $i$ as a function of $E$, analogous to that in Problem 1.12, from (1.3.21), using (1.3.16) as the definition of $E_{1/2}$, for use in solutions that contain both components of a redox couple.

b) Consider the same system as in Problem 1.12, but for a solution containing 10 mM $Ru(NH_3)_6^{3+}$ and 5.0 mM $Ru(NH_3)_6^{2+}$ in 1 M KCl. Use a spreadsheet to calculate the $i$–$E$ curve and plot the results.

c) What is $\eta_{mt}$ at a cathodic current density of 0.48 mA/cm$^2$?

d) Estimate $R_{mt}$.