# BASIC ELECTRICAL PRINCIPLES

# 1

Electrochemical methods of analysis measure electrical quantities in order to yield chemical information. In some cases, the measurement is an electric current (the movement of charge). In other cases, the measurement is a voltage (the amount of energy available to move a charge). Both of these techniques are useful for quantitative analysis of a chemical species, but they can also be used to determine characteristic properties that are useful for qualitative analysis. Some types of qualitative information can be useful for evaluating new materials, such as catalysts.

In describing the fundamentals of electroanalytical methods, this book emphasizes conceptual models. An effort has been made to tie conceptual models of phenomena to basic mathematical relationships in order to provide a foundation to use in reasoning through new situations. Greater insight into electroanalytical phenomena is the intended result. As with other branches of science, new developments displace older techniques. A fundamental understanding of the phenomena upon which electroanalytical tools operate enables one to appreciate the basis for new techniques and related progress in the field. A conceptual understanding also provides a good starting point for learning about other areas of science and technology that involve electrochemical processes. Electrochemical principles play important roles in many natural phenomena and in modern technology [1]. Among these fields are the subjects of energy storage and conversion; biological processes such as cellular action potentials, tissue repair, and growth [2]; electrochemical synthesis; separation technology, nanoparticles, and materials processing in the electronics industry.

Electroanalytical techniques are among the oldest instrumental methods of chemical analysis. They are still widely used for important analyses and are likely to continue to be important for many more decades. Although electroanalytical chemistry is a mature field in many ways, new developments in the realm of selective sensors and the application of electrochemical methods to demanding tasks, such as *in vivo* monitoring of neurotransmitters and remote environmental analysis continue to make instrumental analysis based on electrochemistry relevant. Some attributes of electrochemical analysis that lead to special advantages are summarized in Table 1.1.

Improved detection limits and greater selectivity have led to a greater range of applications. Some methods are capable of quantifying specific analytes down to the picomolar level. Another appealing attribute of electrochemical sensors is that they are relatively easy to miniaturize making them adaptable to a variety of new situations such as *in vivo*

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**TABLE 1.1 Attributes of electroanalytical techniques**

| Attribute | Makes possible |
|---|---|
| Sensitive | Low detection limits |
| Small | *In vivo* monitoring |
| | Measurement in tiny volumes |
| Simple construction | Implantable devices |
| Inexpensive | Mass production |
| | Use in poor communities |
| Simple operation | On-site operation |
| | Health care monitoring |
| | Remote sensing |

monitoring [3]. The sensing element can be very small making it possible to measure quantities of chemical species in tiny volumes or in precise locations, such as at the terminus of a single neuron. Electrochemical methods usually require only very simple accessories. That makes them portable and, in some cases, it makes medical implantation of the sensor possible. Sensors can often be made of inexpensive materials that can be mass produced making them attractive for personal healthcare monitors, such as the handheld glucose monitor used by millions of people to manage their diabetes [4]. Other electroanalytical instruments are capable of a wide range of experiments making them well-suited to studying organic reaction mechanisms associated with electron transfer.

Before launching into the principles of electrochemistry, it is appropriate to say a word about the structure of this book. Chapter summaries appear at the beginning of each chapter in the form of an overview. Unlike reading a novel, here it is helpful for you to know the plot in advance. It helps you to know what to take away from the story. It is worthwhile to read the overview both before and after reading the other sections of the chapter. This book is aimed at students of instrumental analysis, but it is also intended to be a solid introduction to electroanalytical principles for any professional scientist. A lot of care has gone into explaining physical mechanisms and underlying concepts. Recent developments leading to new and interesting methods with better performance characteristics and a wide range of applications are described in most chapters. However, there is much more material than can be reasonably absorbed during a typical two-to-three-week unit of a college instrumental analysis course. Therefore, in addition to summarizing the major ideas, these chapter briefings tell you what sections to read, if time is short.

## 1.1. OVERVIEW

This first chapter is a bit different. It serves as an introduction to basic electrical phenomena and should be read in its entirety. Among the important ideas discussed in this chapter are a few definitions. The term "voltage" refers to the electrical potential energy of a charged particle. It is a measure of the force of attraction or repulsion on a single charged particle by the local density of charges in the neighborhood. The density of charges in the earth itself is thought to be reasonably constant and, as such, provides a local reference point for

electrical energy. Instruments are often attached to a conductor in contact with the earth. This reference point is often referred to as "ground," and it is considered to be a point representing 0 V.

One volt equals one joule per coulomb of charge. The charge on a mole of electrons is $9.6485 \times 10^4$ C/mol. This number shows up in a lot of electrochemical relationships and is called the Faraday, $F$, after the nineteenth-century scientist, Michael Faraday. Faraday established the relationship between charge, $Q$, transferred in an electrochemical reaction, such as the reduction of silver ions to silver metal, and the number of moles of reactant, $N$. This is Faraday's law: $Q = nFN$, where $n$ is the number of moles of electrons transferred per mole of reactant. Another important concept is the free energy, $\Delta G$, that drives an electrochemical reaction. The free energy of an electrochemical system is proportional to the voltage, $E$, and is a measurable quantity, $\Delta G = -nFE$.

Electrical current is the movement of charge and is analogous to current in a river. While a river's current is measured in the volume flow rate of the water, electrical current is measured in amperes. One ampere is equivalent to a coulomb of charge moving past a given point per second. Electrons carry charge in electrical circuits. Ions carry charge in solution. Although electrons are negatively charged, current is defined as though positive charges are moving in a circuit. The direction of the current, then, is defined as movement of charge from a higher potential to a lower potential.

Electrochemical experiments are performed in containers called cells in which two or more electrodes connect the cell to an outside electrical circuit that allows one to measure the voltage and/or the current during the experiment. Potentiometric methods measure the voltage (that is, potential) between electrodes without the passage of a significant amount of current. No significant chemical changes occur in a properly performed potentiometric experiment. In Chapter 2, the Nernst equation that relates potential in a potentiometric experiment to the activity of an analyte is discussed. An activity is the effective reactant concentration of a species. An activity of a species is proportional to its concentration, $C_i$. $a_i = \gamma_i \cdot C_i$, where the proportionality constant, $\gamma_i$, is known as an activity coefficient and is dependent upon the ionic strength of the solution. In contrast, voltammetric methods deliberately apply energy in the form of a voltage from an outside source to a cell in order to drive a chemical reaction at a working electrode. In these experiments, the current is related to the number of moles of reactant that is converted in the process. This current can be used to quantify the concentration of the original reactant.

In addition to the working electrode (or an indicator electrode in a potentiometric experiment), a second electrode is needed to transfer electrons into or out of the cell in order to counterbalance the charge going into or out of the solution at the working or indicator electrode. This second electrode is a reference electrode. It exploits a simple, reliable electron transfer process that occurs at a well-established voltage. The reference electrode is designed to maintain its potential (voltage) in the process. Consequently, all of the energy applied to the cell from the outside is focused onto the working electrode. Whenever the current level or the cell's electrical resistance, $R$, is high, some energy is lost as heat in overcoming the electrical resistance of the solution. This causes an error in voltammetric experiments because some voltage is lost from the voltage that was intended to be applied to the working electrode. This error can be calculated from Ohm's law, $V_{lost} = iR_{cell}$.

Interesting things happen at the boundary of any two phases. Charges, either electrons or ions, can cross these boundaries leading to an excess of electrical charge accumulating on one side and a layer of charge of opposite sign accumulating on the other side. This double layer of charge leads to a difference in electrical potential energy across the interface. This is the potential energy measured in potentiometric experiments that is related to the activity of the analyte ion. In voltammetric experiments, the boundary potential between an electrode and the solution controls the rate of the electron transfer between the analyte in solution and the working electrode.

An electrical capacitor serves as a good model for many aspects of the electrical double layer. The charge, $Q$, on either side of the double layer can be calculated from $Q = CV$, where $V$ is the voltage or potential difference across the double layer and the coefficient, $C$, is the capacitance. There are subtleties to the structure of the double layer that have significance to electron transfer studies, but most of the charge on the solution side accumulates in a layer called the outer Helmholtz plane (OHP), where ions are separated from the electrode by a layer of one or two water molecules.

The conductance of a solution is the reciprocal of the solution's electrical resistance. Its magnitude depends on the type and concentration of the ions. The measurement of the conductance of a water sample is a semiquantitative measure of ionic concentration. Conductance is also used as a special detector for ionic solutes in ion chromatography.

Mass transport is a term for the movement of a chemical species in solution. Two mechanisms for material movement are very important to electroanalytical chemistry. The net movement in a given direction that is due to a concentration gradient and is characterized by a random walk of the molecule or the ion in an unstirred solution is known as diffusion. The flux, $J_i$, of a species is a measure of the net movement of material across a plane perpendicular to the direction of movement. It has units of mol/cm$^2$/s. Fick's first law of diffusion associates the flux to the concentration gradient for the species. $J_i = D_i(\partial C_i/\partial x)$. This is a key concept in electron-transfer experiments. The other mechanism for mass transport is convection or stirring of the bulk solution.

In both voltammetry and potentiometry experiments, a difference in rates of diffusion associated with salt bridges used with reference electrodes leads to a higher flux for either positive or negative ions over those of the opposite charge. The excess of charge "pushes back" against continuing build-up of charge leading to a steady state situation. The result is a net separation of charge and a junction potential or diffusion potential. Junction potentials are generally small, but they can be serious errors in potentiometric experiments. Later chapters discuss this issue in depth.

$$E_{\text{measured}} = E_{\text{indicator electrode}} - E_{\text{reference electrode}} + E_{\text{junction}}$$

## 1.2. BASIC CONCEPTS

Electrical phenomena are associated with charged particles. Electrons are the most common charge carriers that one encounters, but ions in a solution are also important charge carriers. The purpose of this chapter is to define some electrochemical terms and introduce some fundamental concepts associated with electrical charge and phase boundaries.

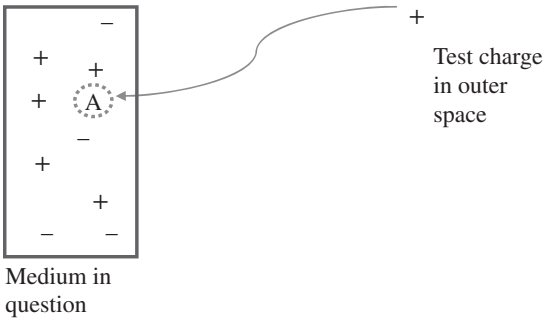


**FIGURE 1.1** The electric (or electrostatic) potential energy at a point, A, in a given medium is a measure of the net energy required or released in moving a test charge from outer space (where it is assumed to be free of forces to interact with) to point A where other charges attract or repel it.

All electrochemical techniques involve measuring (and sometimes manipulating) the voltage at an electrode. What is voltage? Voltage is a measure of the electrical energy available to do work on a charged particle. A charged particle has an electric field associated with it that interacts with its environment. An electric field is the force that two charged particles experience as a function of distance between them. Charges with the same sign repel each other and charges of opposite sign attract. Consequently, the arrangement of charged particles surrounding a given location will determine whether a charged particle coming into that place from the outside will be stabilized by net attractive forces or will be destabilized by net repulsive forces. The electric potential energy for a charged particle is defined as the energy spent or released in the process of inserting a positive test charge into a specific environment. For example, consider an arbitrary location in some material, such as point A shown in Figure 1.1.

There exists some collection of charges surrounding the point in question (point A in Figure 1.1). If one were to bring a positively charged particle from outer space, where it is assumed the test charge is free from the influence of any outside electromagnetic fields to point A, one would have to do work (energy would be spent) to overcome other positive charges in the neighborhood. However, if negative charges dominate the neighborhood at point A, there would be a net attractive force on the test charge and energy would be released in moving it from outer space to that position. The energy spent or released in moving a test charge from outer space to point A is the electric potential energy (also known as the electrostatic potential energy) at that point. For simplicity, this energy is often called the potential at point A. If a different arrangement of charges exists at point B (as in Figure 1.2), then moving a test charge from outer space to point B is associated with a different electric potential energy.

There is not a practical way of measuring the absolute electric potential energy at point A or at point B. However, it is possible to measure the electric potential energy difference between points A and B. A common strategy is to define some point in the system under study as a reference point. Then, the potential at any other point in the system is the electric potential energy difference between the point in question and the reference point. In this

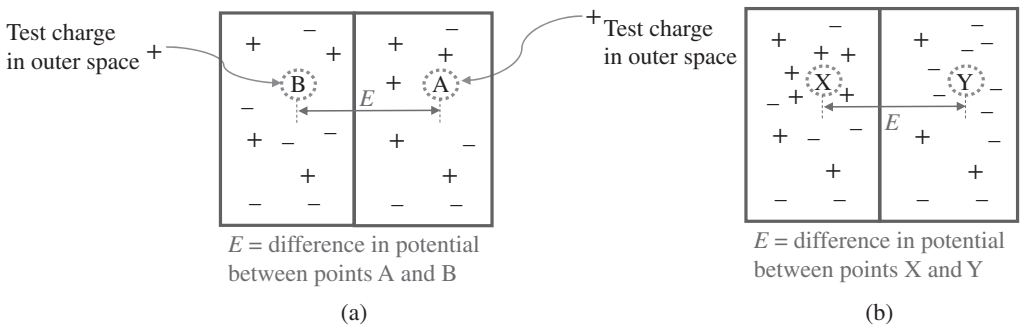


**FIGURE 1.2** a) The absolute electrical potential of a given point cannot be measured. However, the difference in potentials, *E*, between two points, A and B can be measured. In practice, some point within a system is defined as a point of reference so that the potential at any other point can be defined relative to reference point. b) The electric potential for a positive charge around X is much more positive than at Y driving a positive charge from X toward Y or driving a negative charge from Y to X.

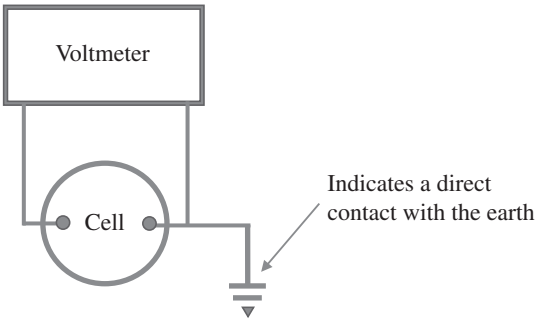


**FIGURE 1.3** Electronic circuits form a continuous loop including all components. Usually some point in the circuit is linked to a conductor that has direct contact with the earth. That point becomes a reference point and is treated as though its potential is 0 V.

approach, no absolute electric potential energies need be evaluated. In the field of electronics, the reference point is often the electric potential energy of a conductor in direct contact with the earth (Figure 1.3). One might say that the electric potential of electrons in the ground is zero, but that is really just a statement about their relative energy; it does not represent an absolute value. (Furthermore, the ground is really just a local benchmark, because small variations in the electrical potential can be found at different places around the earth. Fortunately, a local reference is adequate for most practical situations.).

In electrochemical experiments, the reference potential is established by the use of a reference electrode. It is common practice to refer to a potential or voltage at an electrode when in actuality the value being discussed is the electric potential difference between the electrode in question and the reference electrode being used in that experiment. In older literature, this potential is also called the electromotive force or EMF as it is the energy available to drive charges from one point to the other and do work. Properties of reference electrodes are discussed in chapter 2 (section 2.3.4.3).

### 1.2.1. Volt Defined

In the thought experiment described earlier, a single particle was used as a test charge. The standard definition for electric potential is the energy required to move a unit of positive charge to the position in question. The standard unit of charge in physics is the coulomb and the standard unit of energy is the joule. Electrical energy is measured in volts. One volt represents one joule per coulomb of charge moved.

$$1\,\mathrm{V} = 1\,\mathrm{J/C} \tag{1.1}$$

The volt is the unit of electric potential energy per unit charge that one normally uses with simple meters in the laboratory. So, whenever someone refers to a voltage at some part of their system, they are describing the electric potential difference between that point and some reference point (usually the ground). The voltage is the number of joules released or spent in moving a coulomb of charge from the reference point to the point in question.

It is important to remember that the potential is the electrical work done per unit charge. However, a coulomb is a rather large amount of charge compared to the charge on a single electron. If moving a coulomb of charge from point A to point B costs 1.00 J of energy, then how much energy is required to move a single positively charged particle between the same points? First, one can calculate charge in coulombs/electron using Faraday's constant, $F$, the number of coulombs per mole of electrons, $9.6485 \times 10^4$ C/mol, together with Avogadro's number.

$$\frac{9.6485 \times 10^4\ \mathrm{C/mol}}{6.022 \times 10^{23}\ \mathrm{particles/mol}} = 1.6022 \times 10^{-19}\ \mathrm{C/particle} \tag{1.2}$$

This value is the charge on an electron and is known as the elementary charge. One can calculate the energy that would be required to move a single electron through a voltage difference of 1 V by multiplying the elementary charge by 1 V in the units of 1 J/C:

$$(1.00\,\mathrm{J/C})(1.6022 \times 10^{-19}\ \mathrm{C/particle}) = 1.6022 \times 10^{-19}\ \mathrm{J/particle} \tag{1.3}$$

The result of this calculation is frequently useful and provides the definition for a separate unit of electric potential energy per elementary charge, namely, the electron-volt, eV.

$$1\,\mathrm{eV} = 1.6022 \times 10^{-19}\ \mathrm{J/electron} = 1.6022 \times 10^{-19}\ \mathrm{V} \tag{1.4}$$

### 1.2.2. Current Defined

Current describes the movement of charge. It is the measure of the rate of change in charge moving past a specific observation point.

$$\text{Current} = i = \frac{\partial Q}{\partial t} \tag{1.5}$$

where $Q$ is the charge in coulombs and time, $t$, is in seconds. Current has the units of coulombs per second or amperes.

$$1\,\text{A} = 1\,\text{C/s} \tag{1.6}$$

If one were to make the analogy of an electrical circuit with a river, then the current in amperes or coulombs per second parallels the volume flow rate of the river in gallons per second. The potential energy difference or voltage that is associated with any given component (such as an electrode in an electrochemical experiment) in the electrical circuit, is analogous to the energy available to do work per gallon of water as it drops over a waterfall. Current describes the rate of charge moving (amount per unit of time) and potential is a measure of the energy per unit charge in moving between two points.

### 1.2.3. Oxidation and Reduction

The exchange of electrons between two chemical species is generally known as an oxidation/reduction process or redox reaction. In a redox reaction occurring in a homogeneous solution, one reactant gains electrons while the other reactant loses. It is often useful to consider a redox reaction from the perspective of one of the reactants. Consider a redox reaction between cerium and iron ions in aqueous solution:

$$Ce^{4+} + Fe^{2+} \leftrightarrows Ce^{3+} + Fe^{3+} \tag{1.7}$$

The net reaction equation does not show any electrons as either reactants or products. However, it is useful to separate the two reactants into "half reactions" where electrons do appear.

$$Ce^{4+} + e^{-} \leftrightarrows Ce^{3+} \tag{1.8}$$

$$Fe^{2+} \leftrightarrows e^{-} + Fe^{3+} \tag{1.9}$$

A process in which a chemical species accepts one or more electrons is known as a reduction reaction; a process in which a species loses electrons is an oxidation reaction. Writing the half reactions indicates that the $Fe^{2+}$ ion is being oxidized and the $Ce^{4+}$ ion is being reduced. It also clearly states how many electrons are being transferred per mole of a given reactant.

### 1.2.4. Current and Faraday's Law

In many instrumental electrochemical methods, an electrode surface – usually a metal or carbon conductor – exchanges electrons with the analyte. In those cases, the electrode is treated as an inert source or sink for the electron exchange. The electrode does not appear in the reaction equation. Instead, the electrode reaction appears to be the same as the half reaction for the species being converted. A major benefit of using electrodes in place of a reagent in solution is the fact that the current passing through the electrode can be measured unlike the situation when two chemical species in solution exchange electrons directly. Furthermore, the current is a measure of the amount of analyte reacting.

Whenever electrons are transferred between the analyte and an electrode, the current can be integrated with respect to time in order to obtain the charge, $Q$, transferred.

$$Q = \int i\,\mathrm{d}t \approx i_{\text{average}} * \Delta t \tag{1.10}$$

This charge is related to the moles of oxidized or reduced species by Faraday's law:

$$Q = nFN \tag{1.11}$$

where $n$ = number of moles of electrons transferred per mole of reactant, $N$ is the number of moles of the same reactant that undergo conversion, and $F$ is Faraday's constant, $9.6485 \times 10^4$ C/mol of electrons.

### 1.2.5. Potential, Work, and Gibbs' Free Energy Change

If charge is moved, the amount of work done is proportional to the difference in voltage. Because the voltage difference, $\Delta V$, is the energy spent per unit charge, the total work done in moving the charge, $Q$, is

$$\text{Electrical work} = \left(\frac{\text{energy spent}}{\text{charge}}\right)(\text{number of charges}) = \Delta V * Q \approx \Delta V * (i_{\text{average}} * \Delta t) \tag{1.12}$$

This is analogous to carrying a piano up a flight of stairs. The potential energy difference is fixed by the height of the stairs. To move two pianos requires twice the amount of work.

There are a couple of other conventions worth mentioning here. In electrochemical contexts, $E$ is used instead of $\Delta V$ to represent the electrochemical potential energy difference. It is also common to equate electrical work and the Gibb's free energy change, $\Delta G$. The relationship between potential and $\Delta G$ is usually expressed in terms of the energy per mole of reactant:

$$\Delta G = -nFE \tag{1.13}$$

where $n$ is the number of moles of electrons/mol of reactant, $F$ is Faraday's constant in coulombs/mol of electrons, and $E$ is the potential difference in volts or joules/coulomb. A dimension analysis indicates that $\Delta G$ in Eq. (1.13) has the units of joules per mole of reactant. To find the total energy spent/released, or the total work done, one needs to multiply Eq. (1.13) by $N$, the number of moles of reactant being converted. Also, note that it is a matter of convention that favorable electrochemical processes are assigned positive potentials. Thus, the sign in Eq. (1.13) yields a negative $\Delta G$ for a positive value of $E$ for a favorable process.

Another convention is to define the direction of a current as the direction that the positive charges move. This is the case, despite the fact that electrons are usually the major charge carriers and are moving in the opposite direction. That means that a current flows from a point of a higher potential to a point of lower potential; the electrons move in the opposite direction.

### 1.2.6. Methods Based on Voltage Measurement Versus Current Measurement

Potentiometry is a category of electroanalytical techniques that involves measuring the potential energy difference that develops at the boundary between a sensor and the sample solution as a function of the analyte concentration in the sample solution in which current does not flow. Alternatively, one can use an external power source, such as a battery, to impose a voltage to an electrode surface. This strategy drives an electron transfer reaction between an electrode and analyte in solution at select voltages. Current is measured in these experiments, and it may be proportional to analyte concentration under the right conditions. Voltammetry is a category of methods that measure the current in response to applying a range of voltages to the electrode/solution interface. The term "voltammetry" implies that the voltage is scanned in some manner. If the voltage is held at a constant value while measuring the current, the technique is called amperometry.

## 1.3. ELECTROCHEMICAL CELLS

### 1.3.1. Electrodes

Electroanalytical experiments are built around electrochemical cells (see Figure 1.4). There are some common features to electrochemical cells used for both potentiometry and voltammetry. The signal-generating event occurs at an electrode surface or, more precisely, at the boundary between the sample solution and an electrode surface. In voltammetry experiments, this electrode is often called the working electrode and is made from a metal that is not easily corroded, such as gold or platinum, or a highly conducting form of carbon. In potentiometry experiments, the signal is a voltage that develops at the

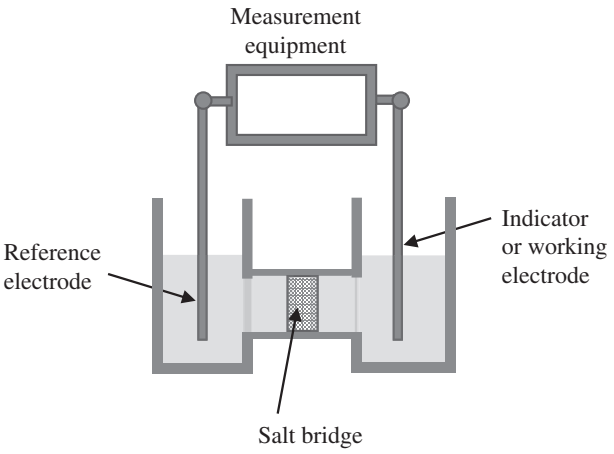


**FIGURE 1.4** Basic arrangement of an electrochemical cell. Two electrodes are required to complete a circuit for the movement of charge. Each electrode is isolated in its own solution (or "half-cell"). A salt bridge keeps the two solutions from mixing but allows some ions to cross in order to complete the electrical circuit. The measurement equipment may be as simple as a voltmeter in a potentiometry experiment or, in the case of a voltammetry experiment, it may include a power source and a current meter.

indicator electrode. The indicator electrode may be as simple as a metal conductor in some experiments, but it is often a more elaborate device. Ideally, no current passes during a potentiometric measurement. The potential being measured is sometimes called the open circuit potential or the rest potential to emphasize the fact that passing a significant amount of current during the measurement can distort the signal. Potentiometric devices are discussed in depth in Chapters 2 and 3.

One electrode is not enough. Measuring current or voltage at an electrode requires that the device be incorporated into an electrical circuit (see Figure 1.4). The external equipment may be as simple as a voltmeter in a potentiometry experiment or a combination of a current meter and a voltage control unit (called a potentiostat) in the case of a voltammetry experiment. The circuit provides a path for charge to move from the external measuring device into the electrochemical cell and back out again to the meter in a complete loop. For example, consider a voltammetry experiment. If the external equipment pushes electrons into the working electrode to drive a reduction reaction (where some chemical species in solution accepts electrons from the electrode), then there must be a mechanism that can return electrons from the cell to the outside circuit to complete the cycle. A second electrode is introduced to provide a path for electrons to return to the meter. This second electrode is known as a reference electrode.

Occasionally, the components of an electrochemical cell are summarized in a schematic diagram written on a single line, such as this:

$$\underset{\text{Anode}}{\mathrm{Cu/Cu^{2+}(5\,mM),\ KNO_3\ (0.1\,M)}}\mathrm{//}\underset{\text{Cathode}}{\mathrm{KCl\ (0.1\,M)/AgCl/Ag}}$$

A single slanted line, /, indicates a phase boundary and a double slanted line, //, indicates a salt bridge separating the two half-cells. A potential may develop at any of those boundaries. The salt bridge may be as simple as a porous glass frit filled with a salt solution. It has two boundaries, one facing each of the two half-cell solution compartments. Components separated by a comma are together in the same solution. Electrode materials are specified at the beginning and the end of the line. The electrode where an oxidation process occurs appears on the left and is known as the anode. The electrode for the half-cell where a reduction process occurs appears on the far right. In this case, a copper electrode is placed in a solution of copper(II) ions together with an electrolyte solution of 0.1 M potassium nitrate. A salt bridge separates the first solution from a potassium chloride solution. In contact with the KCl solution, is a silver wire that has a coating of silver chloride. This particular diagram indicates that the two half-cell reactions are

$$\text{Anode}: \mathrm{Cu} \rightleftarrows \mathrm{Cu^{2+}} + 2\mathrm{e^-}$$

$$\text{Cathode}: \mathrm{AgCl} + \mathrm{e^-} \rightleftarrows \mathrm{Ag} + \mathrm{Cl^-}$$

This type of diagram is more common in energy storage (batteries) and power generation systems, such as fuel cells. In many electroanalytical experiments, an external power source is used to apply a voltage to the system to drive a reaction of interest. In those cases, the applied voltage frequently changes in a manner so that the roles of the electrodes are

reversed one or more times during the experiment. Therefore, such a diagram is only partly informative. A detailed description of the experimental conditions is more appropriate.

In a voltammetry experiment, it is necessary to apply a voltage to the working electrode in order to drive the reaction there. For that reason, it is very important to know how much energy is being applied to the working electrode. Reference electrodes are constructed so that the voltage at their surfaces remains constant. Consequently, any voltage applied to the cell from the outside is completely focused on the interface between the working electrode and the sample solution. A stable reference electrode is also essential for potentiometric experiments where the chemical composition of the solution induces a potential at the indicator electrode. The steadfastness of the reference electrode potential assures the experimenter that voltage changes in the cell represent potential changes of the same magnitude at the indicator electrode. Electrochemists say that the reference electrode is nonpolarizable; it is able to transfer whatever current is needed without budging from its reference potential. How reference electrodes maintain their nonpolarizability is discussed in Chapter 2.

The solution conditions in the immediate environment of the reference electrode are very carefully controlled in order to ensure that the reference electrode potential remains fixed. These conditions are often incompatible with sample solutions. Therefore, the reference solution is frequently isolated from the sample using a salt bridge. This salt bridge is usually a porous ceramic or polymer plug that provides ultrafine pores for the movement of ions but prevents significant mixing between the bulk solutions on opposite sides of the bridge (see Figure 1.4).

In many ways, a potentiometry experiment is simpler than a voltammetry experiment. A pH measurement with a glass electrode is a potentiometric experiment. The chemical composition of the sample solution surrounding the indicator electrode establishes an electrical potential energy difference across the boundary between the indicator electrode and the sample solution. The potential that the voltmeter reads is often called the cell potential, $E_{cell}$. It is common to think about the cell as an assembly of two "half-cells." Usually, the electron-transfer reaction taking place at the reference electrode constitutes one half reaction and the process occurring at the other electrode is the "indicator" half reaction. The measured cell potential represents the difference between the reference and indicator electrode potentials.

$$E_{cell} = E_{indicator} - E_{reference} \quad \text{or} \quad E_{indicator} = E_{cell} + E_{reference} \tag{1.14}$$

In practice $E_{reference}$ is a well-known constant so that any changes in the measured voltage for the cell can be interpreted as changes at the indicator electrode.

### 1.3.2. Cell Resistance

Voltammetry experiments, where currents are measured, require ions in the solution to carry charge between electrodes. Even though water ionizes to a small degree (for pure water $[H^+] = [OH^-] = 10^{-7}$ M), the conductance of water is usually too small for the purposes of most voltammetry experiments. Instead, one usually adds a pure salt to the sample solution. The salt is often referred to as the supporting electrolyte. Because the pH

of a solution influences the electrode reaction in many cases, often an acid/base buffer is also included in the supporting electrolyte. The supporting electrolyte keeps the electrical resistance down. Lower resistance helps minimize voltage errors due to "ohmic losses" in voltammetry experiments. In a voltammetry experiment, current passes through the cell. The solution that carries that current has a finite electrical resistance. Energy, in the form of voltage, is lost overcoming the resistance according to Ohm's law. This loss represents an error in the measurement of the true voltage. The energy lost in volts, $V$, is given by

$$V = iR \tag{1.15}$$

where $i$ is the current driven through the solution resistance, $R$. The actual voltage that reaches the electrode, $V_{\text{actual}}$ is

$$V_{\text{actual}} = V_{\text{applied}} - iR_{\text{cell}} \tag{1.16}$$

In typical voltammetry experiments, the resistance is on the order of 100 Ω. Consequently, errors on the order of 1 mV or bigger occur when the current reaches $10^{-5}$ A ($=10^{-3}$ V/100 Ω) or more. The energy lost in overcoming the solution resistance is energy that is not applied to the working electrode. Whenever the product, $iR$, is greater than a few millivolts, the assumption that all of the energy applied to the cell is focused onto the working electrode/solution interface no longer holds and the data are suspect.

### 1.3.3. Supporting Electrolyte

Supporting electrolyte is also important in potentiometry experiments, even though the current is virtually zero in those experiments. The reason for that is that all potentiometric indicator electrodes respond to the activity of an analyte, not just its concentration. The activity of an ion is a function of the ionic strength of the solution. Recall that the ionic strength, $\mu$, is a measure of the concentration of charge:

$$\mu = \frac{1}{2} \sum c_i z_i^2 \tag{1.17}$$

where $c_i$ is the molar concentration of an ion with charge, $z_i$, summed over all ions. In addition to the effect on activity of the analyte, the mismatch between the sample solution and reference solution in concentration and type of ions making up the supporting electrolyte contributes to an error called the liquid junction potential. (That phenomenon is addressed latter in this chapter.) Consequently, it is important to control the ionic strength. This is often done by the addition of a solution of a high concentration of electrolyte, known as an ionic strength adjustment buffer. Whenever that is not practical, an effort is made to keep the ionic strength constant among all the sample and calibration standards. (Ion activities and activity coefficients are discussed in Appendix A.)

A special voltmeter is used to monitor the potential between the electrodes. In order to function, any electronic meter requires some current to flow. As will be discussed later, drawing a significant level of current through the sensor distorts the voltage signal being measured. Therefore, the goal is to minimize the amount of current that is drawn. The type

of voltmeter that is typically used in a pH meter or other potentiometric apparatus can measure the voltage while preventing a significant amount of current from flowing in the circuit. This attribute is what makes the meter special. Typical voltmeters sold in hardware stores draw current levels of around $10^{-6}$ A. For many electrochemical applications, a level above $10^{-12}$ A can be a significant amount of current. Voltmeters used in potentiometry are designed to draw tiny currents ($10^{-12}$ A or smaller) during operation. They are said to have a high input impedance because they impede the flow of current into the meter.

## 1.4. THE ELECTRIFIED INTERFACE OR ELECTRICAL DOUBLE LAYER

Instrumental methods of electrochemical analysis depend upon chemical events at boundaries between two different phases. In potentiometric experiments, interesting processes give rise to a separation of charge at the boundary between the sample and sensor; in voltammetric experiments an outside power source applies a voltage to the working electrode creating a separation of charge that drives interesting processes there. It is common for charges to appear at many different phase boundaries in nature, for example, at the surface of biological cell walls, on the surface of water droplets or solid aerosols, and at the surface of wet materials such as ceramics, clays, sediments, and soils. The same electrochemical principles that are involved in electrochemical analysis drive lots of natural phenomena as well. One of the most important concepts that is universal is the boundary between two phases where charges accumulate. It is called the electrified interface or the electrical double layer.

### 1.4.1. Structure of the Double Layer

There are numerous electrochemical sensors that selectively respond to a specific chemical species of interest. For example, fluoride is routinely monitored in municipal drinking water by fluoride selective electrodes. Lithium ion can be determined in the blood or urine of a patient being treated for depression by lithium-containing medications using a lithium ion selective electrode. These devices are popular because of their simplicity of use and their reliability. The increasing interest in monitoring select chemical species in clinical, environmental, industrial settings and, more recently, in private homes and for personal health monitoring is likely to encourage the development and implementation of even more sensors of this type.

The heart of all electrochemical sensing devices is the boundary between the sensor and the test solution. It is there that a charge separation develops. Because of its importance, it is very useful to take a closer look at the structure of the boundary. Consider, for example, a metal wire dipping into a salt solution. Assume, for the sake of discussion, that an excess of negative charge (i.e. electrons) appears on the wire. Electromagnetic theory predicts that the excess charge will appear at the surface of the metal. The arrangement of charges on the solution side is a bit more complicated. The excess electrons will naturally attract cations from solution. In the mid-nineteenth century, the German scientist Herman Helmholtz imagined that all of the cations necessary to balance the charge on the metal surface migrate into position at a small distance from the surface forming a plane of charge [5]. It is now known that the cations do not actually come into contact with the

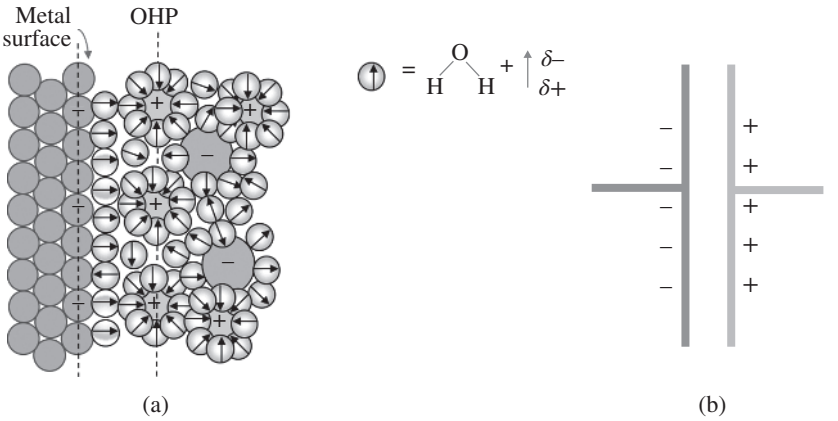


**FIGURE 1.5** The Helmholtz model of the electrified boundary between a metal surface (dark spheres) with a net negative charge and an aqueous salt solution. (a) Cations are attracted to the surface forming a net positive layer to balance the negative charge in the metal. Water molecules occupy the first layer on the metal surface. They also surround ions in solution aligning their dipoles according to the type of charge on the ion. (Arrows point toward the oxygen atoms.) The charges on the solution side define a layer called the outer Helmholtz plane (OHP) [5]. (b) The double layer of charge behaves like a capacitor producing an electrical potential energy difference between the two layers whose magnitude is proportional to the charge.

metal surface because a monolayer of water molecules cling directly to the surface and are not easily displaced. Furthermore, individual cations are surrounded by a sphere of water molecules, known as the hydration sphere, that are also tightly bound. As a consequence, the cations approach the electrode surface no closer than about a distance equal to the length of two water molecules (about 5–6 Å total). Figure 1.5 shows cations with their hydration spheres parked in a line outside a layer of water molecules attached to the electrode surface. The centers of these cations represent a layer now known as the OHP. In the Helmholtz model, the charge on the OHP is equivalent in magnitude to the charge on the metal. This model closely resembles a simple capacitor.

$$Q_{\text{metal}} = -Q_{\text{OHP}} \tag{1.18}$$

In cases where the solid surface has a net positive charge, it attracts an excess of anions to balance the charge and the OHP is occupied by an excess of anions. In some cases, individual anions are able to come into direct contact with the metal surface. This phenomenon is called contact adsorption. Whether or not contact adsorption occurs depends upon the net free energy for three separate steps in the overall adsorption process. Two of the steps are obviously endothermic. Removing water molecules from the electrode surface to make room for the anion and removing part of the hydration sphere around the ion both cost energy. Therefore, only interactions between the ion and the electrode surface that lead to strong bonds make the adsorption process favorable. The electrostatic attractions between oppositely charged ions and the electrode are not decisive by themselves. Contact adsorption relies on London dispersion forces, overlap of electron orbitals, and image forces. An image force is similar to the mechanism known as London dispersion forces where a

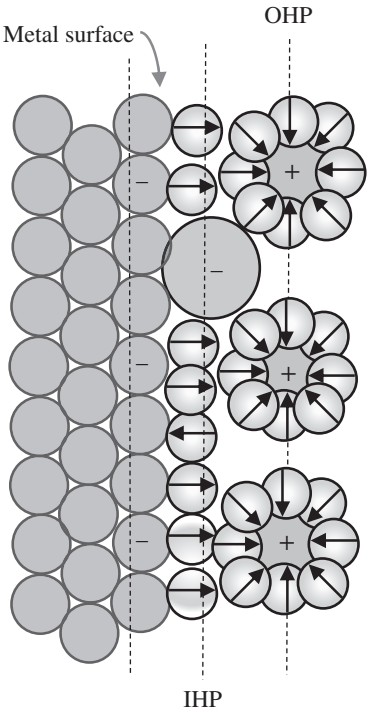


**FIGURE 1.6** The inner Helmholtz plane (IHP) is a plane parallel to the electrode drawn through the center of ions or neutral molecules adsorbed directly in contact with the electrode surface. London and image forces as well as electron overlap between the metal and ion are responsible for the net attraction. These forces can result in binding even when charge considerations oppose adsorption [5].

momentary dipole resulting from the instantaneous arrangement of charge density around a molecule induces a rearrangement of electron density in a neighboring molecule creating a momentary dipole that results in dipole–dipole attraction. Unlike London dispersion forces, the image force is created by a permanent dipole or a charge on the ion inducing a dipole or local excess of charge in the electrode that leads to attraction at that location. The plane that includes the center of ions that are contact-adsorbed to the electrode surface is often called the inner Helmholtz plane (IHP) (see Figure 1.6). An interesting consequence of these additional forces is that some anions can remain attached to the electrode surface even when the electrode is also negatively charged. To account for contact adsorption, the equation for the charge balance becomes

$$Q_{\text{metal}} = -(Q_{\text{IHP}} + Q_{\text{OHP}}) \tag{1.19}$$

The model of Helmholtz suggests that all of the counter ions necessary to balance the charge on the electrode are held rigidly near the electrode surface. However, the experimental evidence suggests that thermal forces are great enough to dislocate counter ions to some degree. These observations inspired work by Louis Gouy [6] and by David Chapman [7] that led to a different model [5]. They proposed that the counter ions are distributed

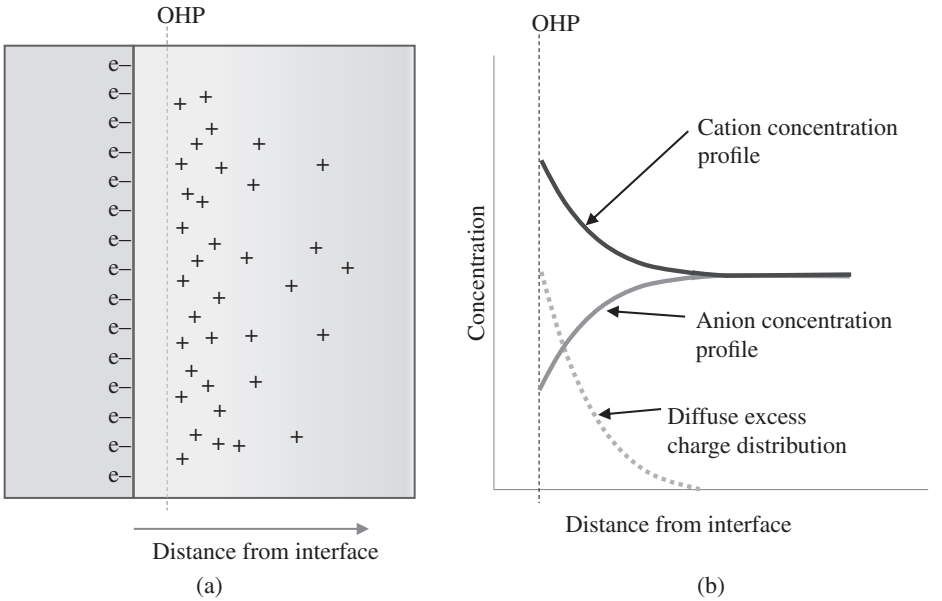


**FIGURE 1.7** (a) Gouy–Chapman model of electrical double layer showing a diffuse region of excess charge on the solution side. (Solvent molecules are not shown for clarity.) (b) The excess concentration drops off exponentially with distance from the electrode surface.

in a nonuniform manner with a high concentration of counter ions near the electrode that falls off exponentially with distance from the electrode surface (Figure 1.7).

Unfortunately, this diffuse–charge model seemed to overcompensate. Experiments indicate that only a fraction of the charge appears to be disrupted by thermal agitation of the surrounding solution, whereas the diffuse charge model implied that it all was susceptible to thermal motion. In 1924, Otto Stern proposed a new model that was a synthesis of the earlier two [8]. Stern proposed that part of the compensating charge on the solution side is held tightly in the IHP plus the OHP and the remaining fraction of charge is contained in a diffuse zone of freely moving counter ions with a concentration that decreases with distance from the electrode surface. The IHP and OHP are sometimes collectively called the Stern layer. This layer is considered a stagnant zone of solution that clings to the surface. Figure 1.8 shows the arrangement of ions at a negatively charged electrode according to the Stern model. The charge balance equation for the double layer becomes

$$Q_{\text{metal}} = -(Q_{\text{IHP}} + Q_{\text{OHP}} + Q_{\text{diffuse}}) = -(Q_{\text{Stern}} + Q_{\text{diffuse}}) \tag{1.20}$$

Notice how the electrical potential changes as a function of distance from the electrode surface. The Stern model has several implications. One is that at higher electrolyte concentrations, the diffuse region of excess counter ions becomes more compact. The distance from the surface to the outer edge of the diffuse region is known as the Debye length, $\lambda_D$. The Debye length is inversely proportional to the square root of the electrolyte concentration. A good benchmark to keep in mind is that the Debye length is about 100 Å (10 nm) for

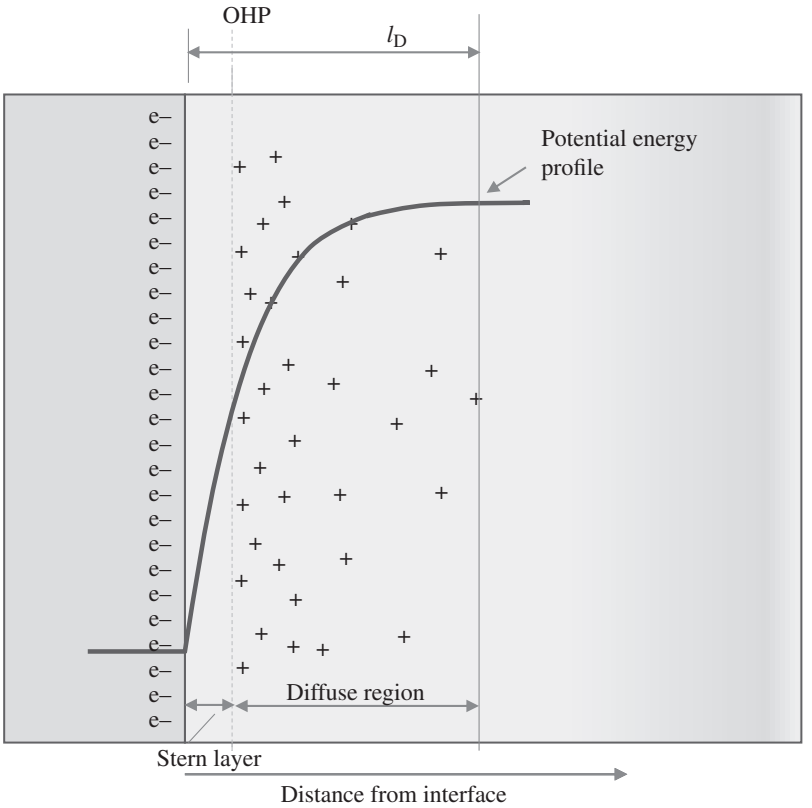


**FIGURE 1.8** Stern model of the electrical double layer. Charges and solvent at the OHP cling to the solid surface. Not all of the charge on the surface of the electrode is compensated by the excess of cations at the outer Helmholtz plane (OHP). A fraction of the counter charge is represented in a diffuse region just beyond the OHP. (Only the charges for the excess cations – the number of cations greater than the local number of anions – are pictured for clarity.)

a sodium chloride solution of 0.01 M [9]. Most electroanalytical measurements are made at electrolyte concentrations of 0.01 M or higher. This profile for the potential has an important significance for voltammetry experiments where molecules must be transported to the electrode surface in order to exchange electrons with the surface. In most cases, the molecules can approach no closer than the OHP. Consequently, the electric potential that they experience is that of the OHP rather than the true potential of the electrode surface. As will be discussed in Chapter 5, this has important implications for the rate of electron transfer and the magnitude of the corresponding current in voltammetry experiments.

It seems appropriate to pause here and note an application of electrochemical principles to phenomena outside of the field of electroanalysis. Naturally occurring phase boundaries involving electrified surfaces often occur in a variety of environments. Here is just one example in which the structure of the electrical double layer is especially relevant. River waters frequently carry tiny soil particles that remain suspended in the water because of the negative charges on the mineral surface (see Figure 1.9). These surface charges arise from the crystal structure in which some $Al^{3+}$ and $Si^{4+}$ ions are replaced

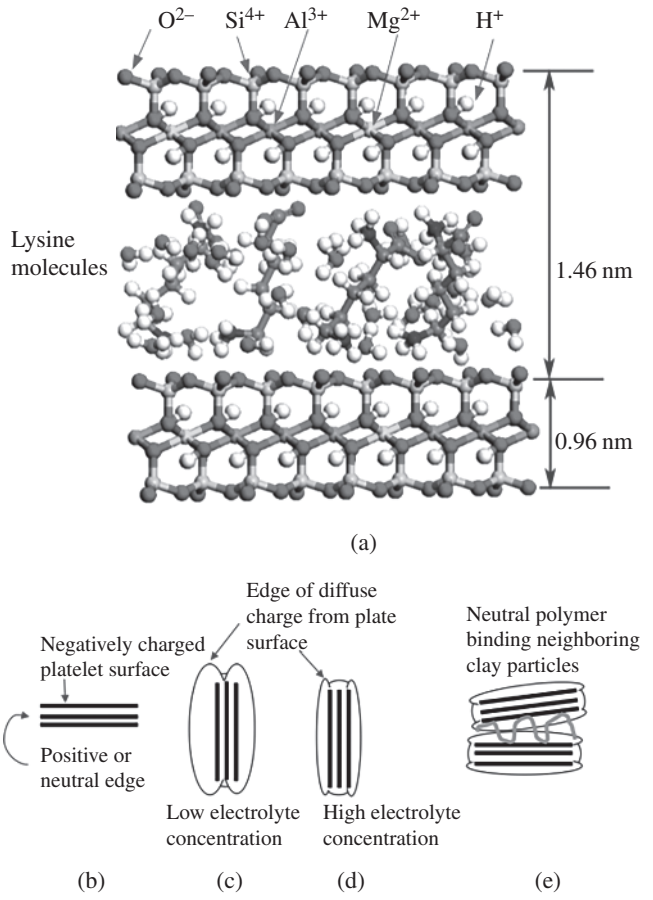


**FIGURE 1.9** The electrical double layer plays an important role in the suspension or sedimentation of tiny particles, such as clay platelets. (a) Montmorillonite clay mineral structure with lysine bridging plates. Source: Adapted with permission from Zhu et al. [17]. Copyright 2019, Elsevier. (b) The surfaces of clay platelets are negatively charged as a result of lower valence cations replacing $Al^{3+}$ and $Si^{4+}$ ions in the crystal lattice. (c) At low ionic concentrations, the diffuse charge region of the sides extends several nanometers out into solution effectively pushing neighboring particles apart. (d) At high electrolyte levels, the field from the diffuse part of the electric double layer compacts allowing clay particles to approach more closely [12]. (e) Neutral polymers, such as naturally occurring polysaccharides, can adsorb at multiple points to neighboring particles leading to aggregation. Aggregation processes are known as coagulation and flocculation.

by lower valence cations, such as $Mg^{2+}$. Cations from the surrounding solution form an electrical double layer with the surface of each clay platelet. In the river, where the electrolyte concentration is low, these charged particles have electrostatic fields that extend far enough into solution to keep neighboring particles from approaching each other closely. However, whenever a river flows into the sea, the ionic strength of the mixture increases suddenly (the sea is about 0.5 M in NaCl) decreasing the distance that the electrostatic field reaches from the surface of a particle. Under these conditions, collisions bring the particles close enough for attractive interactions, such as van der Waals forces and hydrogen

bonding, to overcome the repulsion of the charges. The particles cling to each other and can settle out faster as a result.

Seawater and soil particles are complicated mixtures and multiple mechanisms for binding particles together have been described. In some cases, calcium and other di- or tri-valent cations can bridge between adjacent particles [10]. Another mechanism has been exploited in water treatment and industrial applications of clay materials. Water soluble, neutral polymers, such as polysaccharide chains, are added to clay suspensions in industrial processes to bridge between particles by hydrogen bonding to oxygen atoms in the clay surface [11]. Polymers that attach at several points but still loop out into the solution appear to work best. Presumably, the loops in the chains extend far enough to reach across the electric double layer of neighboring particles. The compression of the electrical double layer is a key part of the mechanism in both industrial and natural processes. As these particles agglomerate at the mouth of rivers, they settle out of solution-carrying nutrients, and sometimes pollutants, into the sediments. This process has very important implications for the ecology of estuaries and the biological productivity of marine environments [12].

### 1.4.2. The Relationship Between Double Layer Charge and the Potential at the Electrode Interface

One can gain a lot of insight about electrochemical processes from approximating the behavior of an electrified interface with that of a capacitor. For example, it is interesting to think about how many charges are involved in creating a voltage across the boundary between two phases. An estimate can be made by modeling the electrical double layer as a simple capacitor where the solid metal constitutes one plate of the capacitor and the solution at the OHP (plus the diffuse region) serves as the second plate (Figure 1.10). (A similar argument can be made for other types of phase boundaries, such as between two ion-containing liquids.)

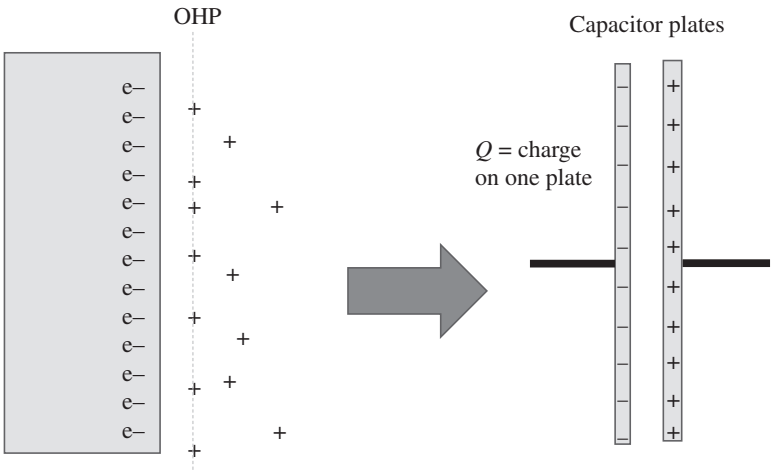


**FIGURE 1.10** The electrical double layer can be modeled as a capacitor where the charge $Q$ is the charge on one plate.

Consider how much charge would be required to create an interface potential difference of 1.0 V. For the sake of discussion, consider a metal surface that has a net positive charge. The magnitude of charge, $Q$, that a capacitor accumulates on each side of the interface for a given voltage, $V$, separating the two plates is given by Eq. (1.21) [5].

$$Q = CV \tag{1.21}$$

where the proportionality constant, $C$, is the capacitance of the dielectric medium separating the plates. (Here is the reason that the model is an over-simplification. The double layer actually has a capacitance that varies with both the electrolyte concentration and with the double layer potential. However, this model does give results that set some upper limits. That is useful.) Empirically, the capacitance of the interface between a metal electrode in an aqueous salt solution is typically in the range of 10–40 μF/cm$^2$ [9]. For convenience, a value at the midpoint of that range will be used, i.e. 25 μF/cm$^2$ or $25 \times 10^{-6}$ C/(V cm$^2$), to estimate the charge in this example. (Notice that the units on the value for the capacitance indicate that total charge depends on the electrode area.)

$$Q = CV = (25 \times 10^{-6}\ \text{C/(V cm}^2))(1\ \text{V}) = 25 \times 10^{-6}\ \text{C/cm}^2 \tag{1.22}$$

Because there are $9.6485 \times 10^4$ C/mole of charge:

$$Q, \text{in moles of charge} = \frac{25 \times 10^{-6}\ \text{C/cm}^2}{9.6485 \times 10^4\ \text{C/mol}} \approx 2.5 \times 10^{-10}\ \text{moles of charge/cm}^2 \tag{1.23}$$

The calculation indicates that $2.5 \times 10^{-10}$ mol of anions will be required to charge the double layer to a potential of 1.0 V. Thus, on a mole basis, the number of ions required to charge the solution side of the interface is tiny. For comparison, consider the number of moles of anions present next to a square electrode 1 cm on a side. Consider the chloride ions in a volume of 1 cm$^3$ solution of 0.1 M NaCl.

$$\text{Moles chloride ions} = 0.1\ \text{mol/l}(1 \times 10^{-3}\ \text{l}) = 1 \times 10^{-4}\ \text{mol} \tag{1.24}$$

$$\frac{2.5 \times 10^{-10}\ \text{moles of charge in double layer}}{10^{-4}\ \text{mol Cl}^-\ \text{ions in 1 ml}} = 2.5 \times 10^{-6} = 0.000\,25\% \tag{1.25}$$

Charging the electrode to 1.0 V would require less than 0.0003% of the chloride ions from the surrounding milliliter of solution to be recruited into the double layer. Clearly, that amount represents a negligible loss to the $Cl^-$ concentration in the neighboring solution.

For every potential difference that appears across the double layer, there is a corresponding arrangement of charge. If the number of charges changes, the double layer potential changes. Likewise, if one is applying a voltage to the interface, then one must move electrons and ions to establish any new arrangement of charge. Because the movement of charge constitutes a current, then a current will exist until the new arrangement of charge is established. This phenomenon is called the double layer charging current. It can be a problem in some voltammetry experiments, because the signal current may be

much smaller than the double layer charging current. In applied potential techniques one is usually interested in measuring the current that is related to the amount of analyte that is being oxidized or reduced at the electrode interface. The signal current associated with the oxidation or reduction of a chemical species is called a Faradaic current because the charge exchanged between the electrode and the electroactive species in solution is proportional to the number of moles of analyte that is oxidized or reduced according to Faraday's law ($Q = \int i\,dt = nFN$). The double layer charging current is non-Faradaic; it represents a background component that one must remove from the signal in order to perform quantitative analyses. Methods for circumventing the double layer charging current are described in Chapter 5 on controlled potential techniques.

## 1.5. CONDUCTANCE

Electrical conductance is a measure of the ability to carry current. Resistance is defined as the reciprocal of conductance. It is easily measurable. Because the measurement of the resistance of a solution depends on the area of the electrodes and the distance separating them, the standard method uses two square platinum plates, 1 cm on each edge separated by 1 cm of solution (see Figure 1.11).

Of course, the interface between the solution and each plate develops an electrical double layer. As a consequence, the electrochemical cell behaves as a circuit with two capacitors in addition to the solution resistance. The resistance is measured using a special meter that applies an oscillating voltage to the electrodes and measures the current response. The resistance component has to be extracted from the response. The resulting resistance is called the specific resistance of the solution, $\rho$, and has the units of $\Omega$ cm. The electrical resistance for any other arrangement of electrodes is proportional to the length, $\ell$, of solution between the electrodes of area, $A$.

$$R = \rho\frac{\ell}{A} \tag{1.26}$$

where $\rho$ is the proportionality constant. Because conductance is inversely related to resistance one can define the conductance, $G$ in Siemens, as follows:

$$G = \kappa\frac{A}{\ell} \tag{1.27}$$

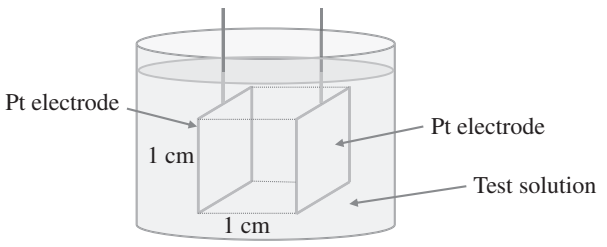


**FIGURE 1.11** Conductance cell.

where $\kappa$ is the electrical conductivity of the solution in units of $\Omega^{-1}$ cm$^{-1}$ or S cm$^{-1}$. Although the standard method defines the shape and separation for electrodes, commercial instruments often have a different geometry and correct for differences by applying a calibration factor.

The solution resistance and conductance also varies with temperature [13].

$$G = \frac{1}{R_{\text{soln}}} = \kappa(1 + r(T - 25)) \tag{1.28}$$

where $T$ = the solution temperature in °C and $r$ is a temperature coefficient in Siemens/degree for the solution. The temperature coefficient needs to be evaluated for different electrolyte solutions, but a representative value is $r = 0.0191$ for a 0.01 M KCl solution [13].

The conductance of a solution also depends on the type of ions that make up the electrolyte. The important point here is that ions move at different speeds. Ions move by diffusion, the process that is conceptualized as a random walk of individual particles, but under the influence of an electric field, they also migrate in the direction of the oppositely charged electrode. The velocity of an ion caused by an electric field is sometimes called the drift velocity or the migration velocity. It is proportional to the strength of the electric field, $\varepsilon$, driving the current.

$$v = u\varepsilon \tag{1.29}$$

where the electric field, $\varepsilon$, has the units of V/cm. It is the voltage difference between the electrodes divided by the distance between them. $v$ is the drift velocity of the ion in cm/s and the proportionality constant, $u$, is the ion mobility. The units for the ion mobility are cm$^2$/(s V). The reason that the mobilities vary among ions is the fact that collisions with solvent molecules and other particles cause drag. Drag is related to the size of the ion. In this context, the size of the ion includes the sheath of solvent molecules that the ion drags with it, its solvent sphere. The bigger the solvated ion, the greater the viscous drag force opposing the ion's movement. All ions are slowed down by the viscosity of the solution. Because the viscosity decreases with temperature, the conductance increases with temperature as indicated in Eq. (1.28). The ion mobility is also proportional to the charge on the ion. Also, the bigger the charge, the greater the tug that the electric field exerts on the ion. Each ion carries a fraction of the total current in proportion to its mobility and its contribution to the total number of charges in solution. An important consequence of the variation in ion mobilities is the fact that the current is shared unevenly among the ions.

There are two practical applications of conductance or conductivity measurements that are of interest to analytical chemists. The first application is a semiquantitative estimate of ion concentration. One can calibrate conductivity measurements for an accurate quantitative determination of a specific salt, if that is the only source of ions in the sample. However, such a situation constitutes a special case. In the area of environmental science and agriculture, conductivity measurements are often made as a general indicator of water purity. Conductivity is also a parameter that is monitored at the outlet of a water purifying system commonly used for analytical and biochemistry laboratories. The quality of the water is often described in terms of the specific resistance. Theoretically, the specific resistance of water with no ions other than those from the dissociation of water is 18.3 MΩ.

There is one common application where conductivity provides good data for quantitative determinations of specific ions. Conductivity detectors are very popular for ion chromatography. In this case, the conductivity cell has been miniaturized so that it can operate on volumes on the microliter scale. Ions eluting from the separation column flow through the electrochemical device and cause a surge in conductance in proportion to their concentration. A full discussion of how a conductivity detector works in liquid chromatography can be found elsewhere [14].

## 1.6. MASS TRANSPORT BY CONVECTION AND DIFFUSION

The movement of ions and molecules in solution is important in many different aspects of electrochemical analysis. The term "mass transport" is often used to mean that reactant material is being driven by some force to the surface of an electrode. The rate at which reactant material is brought to the electrode surface influences the sensitivity of methods in many cases. The two most common mass transport mechanisms are convection and diffusion. In the first case, the bulk solution is mechanically stirred or pushed past an electrode such as in a flowing stream. The term "hydrodynamic system" is also used to mean a flowing or stirred solution that continuously brings material to the electrode.

The other mechanism for mass transport that is exploited in electroanalysis is called diffusion. Diffusion moves material by the force of a concentration gradient. This mechanism is subtler and deserves some discussion here. Imagine two solutions separated by a square window, 1 cm on each edge (see Figure 1.12). Molecules move very rapidly at room temperature, but they are frequently colliding with each other and the solvent. Consequently, the path of any individual molecule changes direction many times per second. The molecule appears to be moving randomly. How fast it moves depends on its solvated radius. Imagine also that one can count the molecules that pass through the window in each direction. The net excess going one direction or the other per second is called the flux for that molecule. A flux has the same dimensions as the product of a concentration and a velocity. The normal units are mol/(cm$^2$ s) (equivalent to mol/cm$^3$ × cm/s). When the concentration for some molecule, M, on both sides of the window is equal, the number going from left to right through the window matches the number going from right to left each second. Consequently, the flux is zero.

Now, imagine starting the experiment over with a concentration of M at a value of $C_M$ on the left side of the window and a concentration of 0 on the right side of the window.

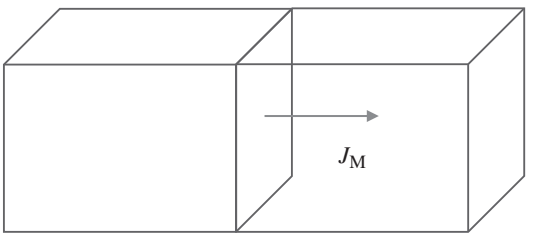


**FIGURE 1.12** The definition of flux is the net number of moles of molecules per second crossing a plane of solution with an area of 1 cm$^2$.

Because there are no molecules on the right side initially, none move through the window from right to left. However, many are going from left to right initially. Consequently, the flux is not zero initially. For ease of discussion, let the direction of left to right represent movement along the $x$-axis in the positive direction. Intuitively, the flux is never going to go from right to left as long as the $C_M$ on the left is greater than it is on the right. It will never be greater on the right. At best, the concentration on the right will reach a value that equals that on the left, but only at equilibrium. Because there are more molecules to consider on the left side, the probability is always greater for a molecule to move from left to right through the window than in the other direction until equilibrium is reached. It also seems intuitive that the bigger the discrepancy in the concentrations on the two sides, the greater the excess in the number of molecules going in one direction. The following equation is a more elegant statement of these ideas. It is known as Fick's first law of diffusion.

$$J_M = -D_M \frac{dC_M}{dx} \tag{1.30}$$

where $J_M$ is the flux of molecule, M, in mol/(cm$^2$ s), $C_M$ is the concentration of M. The proportionality constant, $D_M$, is called the diffusion coefficient in cm$^2$/s. The gradient in concentration is the driving force for moving molecules across the plane perpendicular to the direction of motion. By convention a decreasing concentration in the $x$-direction is represented by a negative gradient, that is $dC/dx < 0$ in that case. The negative sign in front of the diffusion coefficient arises in order to make the flux positive for a concentration that decreases in the direction of increasing $x$. (It is just a convention.) The diffusion coefficient is related to the ion mobility described earlier by the Einstein–Smoluchowski equation [15]:

$$u_i = \frac{|z_i| F D_i}{RT} \tag{1.31}$$

As with ion mobility, the diffusion coefficient decreases with the solvated radius of an ion. The diffusion coefficients for a few ions in water are given in Table 1.2. Note that the

**TABLE 1.2 Diffusion coefficients**

| Ions in water | | |
|---|---|---|
| Ion | Diffusion coefficient[a] (cm$^2$/s) | Hydrated radius[b] (Å) |
| $OH^-$ | $52.73 \times 10^{-6}$ | 3.5 |
| $Na^+$ | $13.34 \times 10^{-6}$ | 4.5 |
| $K^+$ | $19.57 \times 10^{-6}$ | 3 |
| $SO_4^{2-}$ | $10.65 \times 10^{-6}$ | 4 |
| $Ca^{2+}$ | $7.92 \times 10^{-6}$ | 6 |
| $Cl^-$ | $20.32 \times 10^{-6}$ | 3 |
| $Mg^{2+}$ | $7.06 \times 10^{-6}$ | 8 |
| $H^+$ | $96.6 \times 10^{-6}$[c] | 9 |
| $NO_3^-$ | $19.5 \times 10^{-6}$[c] | 3 |

[a]From Samsonl et al. [18]. Copyright 2003. Used with permission.
[b]From Kielland [19]. Copyright 1937, American Chemical Society. Used with permission.
[c]Calculated from the electric mobility given by Bakker [15].

diffusion coefficients for $OH^-$ and $H^+$ are rather large despite the fact that their hydrated radii are also large. That is the case because these ions do not move through water as an individual particle, but rather by exchange of hydrogen ions with molecules of water in their solvation sphere [5].

In a number of different electrochemical methods discussed in later chapters (see section 5.3), a reaction can change the local concentration of a reactant so that the concentration varies in adjacent regions of solution. This difference in concentration drives a net movement of material in the direction of higher to lower concentration.

## 1.7. LIQUID JUNCTION POTENTIALS

Because accuracy in measuring the voltage in potentiometry and in controlling the applied voltage in voltammetry experiments is so important, it is worth noting at this stage a common mechanism that can introduce errors in the cell potential measurement. Most electrochemical measurements involve the use of salt bridges to isolate reference electrodes from the sample solution. The contact between the sample solution and the salt bridge introduces another opportunity for a separation of charge to develop as shown in Figure 1.13. The mechanism for the build-up of a potential is driven by a difference in the mobility of the ions. For example, consider a salt bridge that contains 1 M NaCl as an electrolyte contacting a sample solution with 0.1 M NaCl.

Intuitively, one would expect that a difference in concentration of the ions at the boundary would lead to the movement of ions from the higher concentration toward the medium with the lower concentration. The movement of ions can be modeled mathematically using the Nernst–Planck equation [15]:

$$J_A = -D_A \frac{\partial C_A}{\partial x} - D_A C_A \frac{z_A F}{RT} \frac{\partial \phi}{\partial x} \tag{1.32}$$

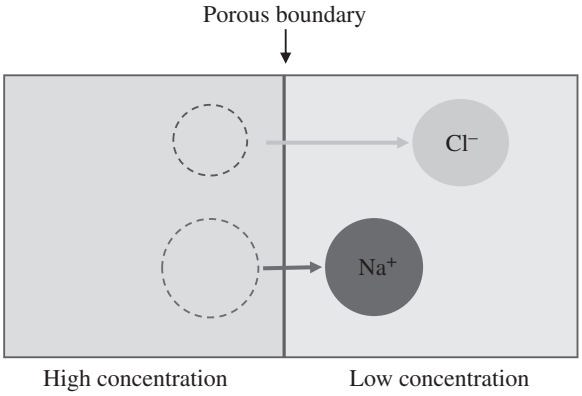


**FIGURE 1.13** A salt bridge is a liquid junction between two solutions that allows a small exchange of ions but prevents the two solutions from mixing. A difference in concentration drives ions from the side of high concentration to the low concentration side. Smaller, faster ions move more charge of one sign across the boundary than the other. The result is a net separation of charge at the boundary causing a voltage difference known as a liquid junction potential.

where $C_A$ is the concentration of solute A in mol/cm$^3$, $D_A$ is the diffusion coefficient of that solute in cm$^2$/s, and $J_A$ is the flux or moles crossing a plane perpendicular to the direction of movement (here, in the $x$-direction) per square centimeters per second, $\frac{\partial \phi}{\partial x}$ is the potential gradient, $F$ is Faraday's constant, and $T$ is the absolute temperature. (Notice that the flux, in mol/(s cm$^2$) has the same dimensions as the product of a concentration and a velocity, mol/cm$^3$ × cm/s.) Initially, both the sodium and chloride ions have the same concentration gradient, and there is no electric potential gradient (and the second term on the right is zero). The faster ion is the one with the larger diffusion coefficient. The diffusion coefficients in water of $Na^+$ and $Cl^-$ are $13.3 \times 10^{-6}$ and $20.3 \times 10^{-6}$ cm$^2$/s, respectively. That suggests that the chloride moves about 50% faster than the sodium ion. Consequently, a negative charge builds up on the lower concentration (sample solution) side and an equal amount of positive charge accumulates on the salt bridge side of the boundary due to the excess of sodium lagging behind. As a result, this process creates a potential energy difference across the boundary. However, the process quickly reaches a steady-state potential. The potential gradient across the boundary (the second term in Eq. (1.32)) is no longer zero. The potential gradient accelerates the movement of cations and decelerates the movement of anions so that the cation flux and anion flux become equivalent. This mechanism leads to the liquid junction potential. This junction potential is a part of the measured cell potential and it changes with solution conditions.

$$E_{cell} = E_{measured} = E_{indicator} + E_{junction} - E_{reference} \tag{1.33}$$

The junction potential can introduce errors as big as 50 mV or more [16]. A useful equation for calculating the magnitude of this junction potential was presented by Henderson and is discussed in Appendix C.

Figure 1.14 can guide one's thinking about junction potentials in order to determine the effect on the measured cell potential. The reference point is the reference electrode. Going from the potential of the reference electrode through the electrochemical cell to the

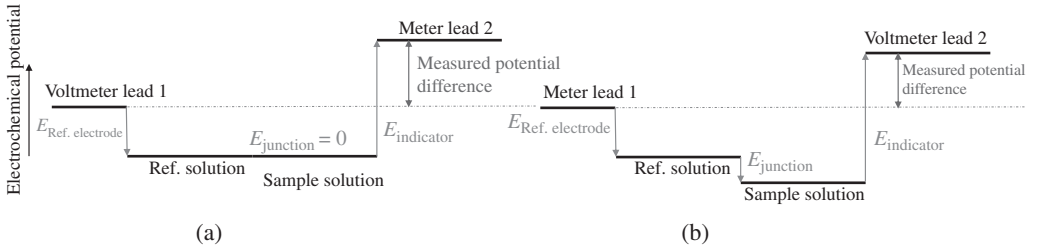


**FIGURE 1.14** The measured potential between the indicator and reference electrodes includes all of the transitions in potential in between, represented by vertical arrows in the diagram. If anions are moving across the salt bridge faster than cations in the direction of the reference solution toward the sample solution, then $E_{junction}$ is negative; the vector for the potential for the junction is downward. (The sample solution potential is lower than that of the reference solution.) In this case, the $E_{indicator}$ is positive, so it is represented by an upward vector going from the solution potential toward the second meter lead. The cell potential is the value measured between the two voltmeter leads. If the junction potential had the opposite sign, then the vector for the junction would be upward and the measured potential would be larger than shown here. Both situations yield values that are different than the ideal (when $E_{junction} = 0$). (a) Ideal case and (b) real case; $E_{junction} \neq 0$.

other side, the path crosses the salt bridge. The argument above indicated that the sample solution will be at a lower potential (more negative) than the reference solution. The path from there, across the indicator electrode interface, starts from this solution potential which appears lower than it would have in the absence of a junction potential. The measured cell potential is indicated as a vector sum for all the transitions in potential between the meter leads. Ideally, the measured voltage is merely a difference between the reference and indicator electrode potentials, but the junction potential must also be included. The diagram indicates that the junction potential would be a negative number in Eq. (1.33). That is, the junction potential leads to an error that makes the measured potential appear more negative (or less positive) in this situation.

Of course, one way to avoid this error is to keep the conditions (other than the analyte concentration) of the sample solution and standards as similar as possible. This concern is another reason for using an ionic strength buffer. A further precaution that minimizes the junction potential is to use an electrolyte for both the salt bridge and test solutions in which the cation and anion have very similar diffusion coefficients, such as KCl. Potassium ions have a diffusion coefficient in water of $19.6 \times 10^{-6}\,\text{cm}^2/\text{s}$ which is very similar to that of chloride ions ($20.3 \times 10^{-6}\,\text{cm}^2/\text{s}$).

There is another consideration in setting up a salt bridge. Despite carefully matched diffusion coefficients, another mechanism can give rise to a junction potential. Glass or ceramic material are often used to make porous frits for salt bridges. These materials usually have a net negative charge on their surfaces. For glass with pores on the order of 5–10 nm in diameter, the negative charge can effectively screen anions from crossing the boundary leading to a junction potential on the order of 50 mV even with KCl as a supporting electrolyte (see Figure 1.15). Consequently, salt bridges made from material with larger (micron size) pores are preferable [16]. The trade-off is a greater leakage of ions from the salt bridge into the sample.

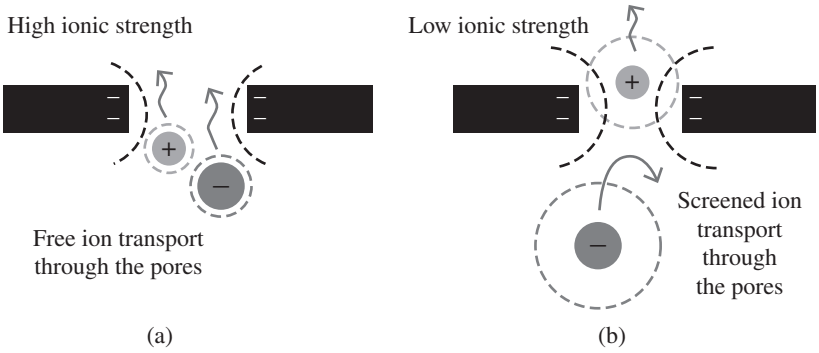


**FIGURE 1.15** Microscopic pores in a glass frit used as a salt bridge. The electric field (shown by dashed lines) from negative charges on the glass surface extends a few nanometers into the surrounding solution. This distance is called the Debye length of the electrostatic field. The Debye length is inversely dependent on the ionic strength. (a) At high ionic strength, the anion can pass through the pore without its field interacting with that of the glass. (b) At low ionic strength, the field of the anion and the charge on the glass repel each other decreasing the migration of anions through the pore. Source: Adapted with permission from Mousavi et al. [16]. Copyright 2016, American Chemical Society.

## PROBLEMS

**1.1** A bourbon distillery treats its discharge water (that remains behind after the whisky distills off) electrochemically to remove copper by plating it out on an electrode. After 42 days of continuous operation the electrode was replaced. It was weighed before sending it off to a copper recycling service and was found to have recovered 450 g of copper. Calculate the average current during its use assuming that 100% of the current was used in the reduction of $Cu^{2+}$ to Cu metal.

**1.2** Consider a carbon electrode with a circular shape and a diameter of 3.0 mm dipping into a 0.1 M NaCl solution with a double layer capacitance of 20 μF/cm$^2$. If the electrode receives a pulse of $1.0 \times 10^{12}$ electrons, what will the change in voltage be at the electrode solution interface.

**1.3** The diffusion coefficient for $NO_3^-$ ion is bigger than the diffusion coefficient for $Na^+$ ion. Consider measuring the electrochemical cell potential in which a salt bridge is used between the reference solution containing 3 M $NaNO_3$ and a sample containing 0.1 M $NaNO_3$ supporting electrolyte solution. Explain whether there will be a junction potential and, if so, whether the cell potential with the junction potential will appear more positive or more negative than without it.

**1.4** Explain why ohmic loss is more likely to cause a serious error in a voltammetry experiment than it is for a potentiometric experiment.

**1.5** If 250 μA of current flows when a potentiostat applies −0.351 V to an electrochemical cell with a resistance of 152 Ω, what is the ohmic loss in voltage?

**1.6** Explain two different mechanisms that could cause the potential of a pH electrode to shift upon the addition of 3 g of KCl to 100 ml of a solution of 0.1 M HCl.

**1.7** How many moles of electrons would be required to change the voltage on a Pt circular disk electrode with a 2.0 mm diameter from −0.100 to −0.500 V in an electrolyte solution of 0.1 M KCl given the electrode solution capacitance of 24 μF/cm$^2$?

**1.8** The average thermal energy (or the average kinetic energy) in three dimensions for a molecule is often give as $3/2\,kT$ where $k$ is Boltzmann's constant and $T$ is the absolute temperature. How does the average thermal energy of a molecule at 25 °C compare with 1 eV?

**1.9** How does the energy of a blue photon at 400 nm compare to 1 eV?

**1.10** How does the dissociation energy of the carbon–carbon bond in an ethane molecule compare with 1 eV?

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