11: ELECTROCHEMICAL METHODS

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CHAPTER OVERVIEW

11: ELECTROCHEMICAL METHODS

In Chapter 10 we examined several spectroscopic techniques that take advantage of the interaction between electromagnetic radiation and matter. In this chapter we turn our attention to electrochemical techniques in which the potential, current, or charge in an electrochemical cell serves as the analytical signal.

Although there are only three fundamental electrochemical signals, there are many possible experimental designs—too many, in fact, to cover adequately in an introductory textbook. The simplest division of electrochemical techniques is between bulk techniques, in which we measure a property of the solution in the electrochemical cell, and interfacial techniques, in which the potential, current, or charge depends on the species present at the interface between an electrode and the solution in which it sits. The measurement of a solution's conductivity, which is proportional to the total concentration of dissolved ions, is one example of a bulk electrochemical technique. A determination of pH using a pH electrode is an example of an interfacial electrochemical technique. Only interfacial electrochemical methods receive further consideration in this chapter.

11.1: OVERVIEW OF ELECTROCHEMISTRY

The focus of this chapter is on analytical techniques that use a measurement of potential, current, or charge to determine an analyte's concentration or to characterize an analyte's chemical reactivity. Collectively we call this area of analytical chemistry ***electrochemistry*** because its originated from the study of the movement of electrons in an oxidation–reduction reaction.

Despite the difference in instrumentation, all electrochemical techniques share several common features. Before we consider individual examples in greater detail, let's take a moment to consider some of these similarities. As you work through the chapter, this overview will help you focus on similarities between different electrochemical methods of analysis. You will find it easier to understand a new analytical method when you can see its relationship to other similar methods.

FIVE IMPORTANT CONCEPTS

To understand electrochemistry we need to appreciate five important and interrelated concepts: (1) the electrode's potential determines the analyte's form at the electrode's surface; (2) the concentration of analyte at the electrode's surface may not be the same as its concentration in bulk solution; (3) in addition to an oxidation–reduction reaction, the analyte may participate in other chemical reactions; (4) current is a measure of the rate of the analyte's oxidation or reduction; and (5) we cannot control simultaneously current and potential.

> The material in this section—particularly the five important concepts—draws upon a vision for understanding electrochemistry outlined by Larry Faulkner in the article "Understanding Electrochemistry: Some Distinctive Concepts," *J. Chem. Educ.* **1983**, *60*, 262–264. See also, Kissinger, P. T.; Bott, A. W. "Electrochemistry for the Non-Electrochemist," *Current Separations*, **2002**, *20:2*, 51–53.

THE ELECTRODE'S POTENTIAL DETERMINES THE ANALYTE'S FORM

In Chapter 6 we introduced the ladder diagram as a tool for predicting how a change in solution conditions affects the position of an equilibrium reaction. Figure 11.1.1 , for example, shows a ladder diagram for the Fe^{3+}/Fe^{2+} and the Sn^{4+}/Sn^{2+} equilibria. If we place an electrode in a solution of Fe^{3+} and Sn^{4+} and adjust its potential to +0.500 V, Fe^{3+} is reduced to Fe^{2+} but Sn^{4+} is not reduced to Sn^{2+}.

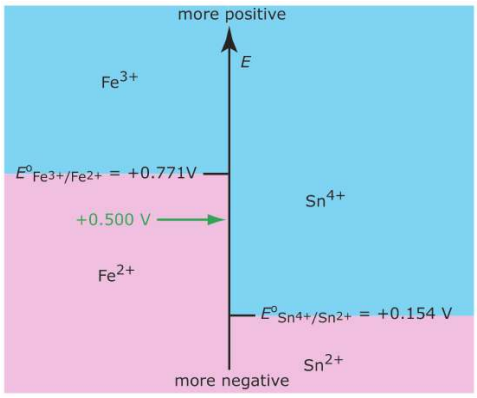


Figure 11.1.1 . Redox ladder diagram for Fe^{3+}/Fe^{2+} and for Sn^{4+}/Sn^{2+} redox couples. The areas in blue show the potential range where the oxidized forms are the predominate species; the reduced forms are the predominate species in the areas shown in pink. Note that a more positive potential favors the oxidized forms. At a potential of +0.500 V (green arrow) Fe^{3+} reduces to Fe^{2+}, but Sn^{4+} remains unchanged. You may wish to review the earlier treatment of oxidation–reduction reactions in Chapter 6.4 and the development of ladder diagrams for oxidation–reduction reactions in Chapter 6.6.

INTERFACIAL CONCENTRATIONS MAY NOT EQUAL BULK CONCENTRATIONS

In Chapter 6 we introduced the Nernst equation, which provides a mathematical relationship between the electrode's potential and the concentrations of an analyte's oxidized and reduced forms in solution. For example, the Nernst equation for Fe^{3+} and Fe^{2+} is

$$E = E_{Fe^{3+}/Fe^{2+}} - \frac{RT}{nF}\ln\frac{[Fe^{2+}]}{[Fe^{3+}]} = \frac{0.05916}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} \quad (11.1.1)$$

where E is the electrode's potential and $E^{\circ}_{Fe^{3+}/Fe^{2+}}$ is the standard-state reduction potential for the reaction $Fe^{3+}(aq) \rightleftharpoons Fe^{2+}(aq) + e^{-}$. Because it is the potential of the electrode that determines the analyte's form at the electrode's surface, the concentration terms in Equation 11.1.1 are those of Fe^{2+} and Fe^{3+} at the electrode's surface, not their concentrations in bulk solution.

This distinction between a species' surface concentration and its bulk concentration is important. Suppose we place an electrode in a solution of Fe^{3+} and fix its potential at 1.00 V. From the ladder diagram in Figure 11.1.1 , we know that Fe^{3+} is stable at this potential and, as shown in Figure 11.1.2 a, the concentration of Fe^{3+} is the same at all distances from the electrode's surface. If we change the electrode's potential to +0.500 V, the concentration of Fe^{3+} at the electrode's surface decreases to approximately zero. As shown in Figure 11.1.2 b, the concentration of Fe^{3+} increases as we move away from the electrode's surface until it equals the concentration of Fe^{3+} in bulk solution. The resulting concentration gradient causes additional Fe^{3+} from the bulk solution to diffuse to the electrode's surface.

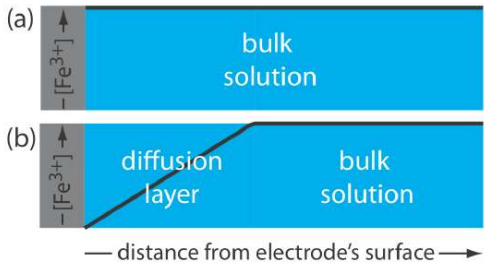


Figure 11.1.2 . Concentration of Fe^{3+} as a function of distance from the electrode's surface at (a) E = +1.00 V and (b) E = +0.500 V. The electrode is shown in gray and the solution in blue.

We call the region of solution that contains this concentration gradient in Fe^{3+} the diffusion layer. We will have more to say about this in Chapter 11.4.

THE ANALYTE MAY PARTICIPATE IN OTHER REACTIONS

Figure 11.1.1 and Figure 11.1.2 shows how the electrode's potential affects the concentration of Fe^{3+} and how the concentration of Fe^{3+} varies as a function of distance from the electrode's surface. The reduction of Fe^{3+} to Fe^{2+}, which is governed by Equation 11.1.1, may not be the only reaction that affects the concentration of Fe^{3+} in bulk solution or at the electrode's surface. The adsorption of Fe^{3+} at the electrode's surface or the formation of a metal–ligand complex in bulk solution, such as $Fe(OH)^{2+}$, also affects the concentration of Fe^{3+}.

CURRENT IS A MEASURE OF RATE

The reduction of Fe^{3+} to Fe^{2+} consumes an electron, which is drawn from the electrode. The oxidation of another species, perhaps the solvent, at a second electrode is the source of this electron. Because the reduction of Fe^{3+} to Fe^{2+} consumes one electron, the flow of electrons between the electrodes—in other words, the current—is a measure of the rate at which Fe^{3+} is reduced. One important consequence of this observation is that the current is zero when the reaction $\mathbf{Fe^{3+}}(aq) \rightleftharpoons \mathbf{Fe^{2+}}(aq) + e^-$ is at equilibrium.

The rate of the reaction $\mathbf{Fe^{3+}}(aq) \rightleftharpoons \mathbf{Fe^{2+}}(aq) + e^-$ is the change in the concentration of Fe^{3+} as a function of time.

WE CANNOT CONTROL SIMULTANEOUSLY BOTH THE CURRENT AND THE POTENTIAL

If a solution of Fe^{3+} and Fe^{2+} is at equilibrium, the current is zero and the potential is given by Equation 11.1.1. If we change the potential away from its equilibrium position, current flows as the system moves toward its new equilibrium position. Although the initial current is quite large, it decreases over time, reaching zero when the reaction reaches equilibrium. The current, therefore, changes in response to the applied potential. Alternatively, we can pass a fixed current through the electrochemical cell, forcing the reduction of Fe^{3+} to Fe^{2+}. Because the concentrations of Fe^{3+} decreases and the concentration of Fe^{2+} increases, the potential, as given by Equation 11.1.1, also changes over time. In short, if we choose to control the potential, then we must accept the resulting current, and we must accept the resulting potential if we choose to control the current.

CONTROLLING AND MEASURING CURRENT AND POTENTIAL

Electrochemical measurements are made in an electrochemical cell that consists of two or more electrodes and the electronic circuitry needed to control and measure the current and the potential. In this section we introduce the basic components of electrochemical instrumentation.

The simplest electrochemical cell uses two electrodes. The potential of one electrode is sensitive to the analyte's concentration, and is called the ***working electrode*** or the ***indicator electrode***. The second electrode, which we call the ***counter electrode***, completes the electrical circuit and provides a reference potential against which we measure the working electrode's potential. Ideally the counter electrode's potential remains constant so that we can assign to the working electrode any change in the overall cell potential. If the counter electrode's potential

is not constant, then we replace it with two electrodes: a ***reference electrode*** whose potential remains constant and an ***auxiliary electrode*** that completes the electrical circuit.

Because we cannot control simultaneously the current and the potential, there are only three basic experimental designs: (1) we can measure the potential when the current is zero, (2) we can measure the potential while we control the current, and (3) we can measure the current while we control the potential. Each of these experimental designs relies on ***Ohm's law***, which states that the current, i, passing through an electrical circuit of resistance, R, generates a potential, E.

$$E = iR$$

Each of these experimental designs uses a different type of instrument. To help us understand how we can control and measure current and potential, *we will describe these instruments as if the analyst is operating them manually*. To do so the analyst observes a change in the current or the potential and manually adjusts the instrument's settings to maintain the desired experimental conditions. It is important to understand that modern electrochemical instruments provide an automated, electronic means for controlling and measuring current and potential, and that they do so by using very different electronic circuitry than that described here.

> This point bears repeating: It is important to understand that the experimental designs in Figure 11.1.3 , Figure 11.1.4 , and Figure 11.1.5 do not represent the electrochemical instruments you will find in today's analytical labs. For further information about modern electrochemical instrumentation, see this chapter's additional resources.

POTENTIOMETERS

To measure the potential of an electrochemical cell under a condition of zero current we use a ***potentiometer***. Figure 11.1.3 shows a schematic diagram for a manual potentiometer that consists of a power supply, an electrochemical cell with a working electrode and a counter electrode, an ammeter to measure the current that passes through the electrochemical cell, an adjustable, slide-wire resistor, and a tap key for closing the circuit through the electrochemical cell. Using Ohm's law, the current in the upper half of the circuit is

$$i_{\text{upper}} = \frac{E_{\text{PS}}}{R_{ab}}$$

where E_{PS} is the power supply's potential, and R_{ab} is the resistance between points a and b of the slide-wire resistor. In a similar manner, the current in the lower half of the circuit is

$$i_{\text{lower}} = \frac{E_{\text{cell}}}{R_{cb}}$$

where E_{cell} is the potential difference between the working electrode and the counter electrode, and R_{cb} is the resistance between the points c and b of the slide-wire resistor. When $i_{\text{upper}} = i_{\text{lower}} = 0$, no current flows through the ammeter and the potential of the electrochemical cell is

$$E_{\text{coll}} = \frac{R_{cb}}{R_{ab}} \times E_{\text{PS}} \tag{11.1.2}$$

To determine E_{cell} we briefly press the tap key and observe the current at the ammeter. If the current is not zero, then we adjust the slide wire resistor and remeasure the current, continuing this process until the current is zero. When the current is zero, we use Equation 11.1.2 to calculate E_{cell}.

Using the tap key to briefly close the circuit through the electrochemical cell minimizes the current that passes through the cell and limits the change in the electrochemical cell's composition. For example, passing a current of 10^{-9} A through the electrochemical cell for 1 s changes the concentrations of species in the cell by approximately 10^{-14} moles. Modern potentiometers use operational amplifiers to create a high-impedance voltmeter that measures the potential while drawing a current of less than 10^{-9} A.

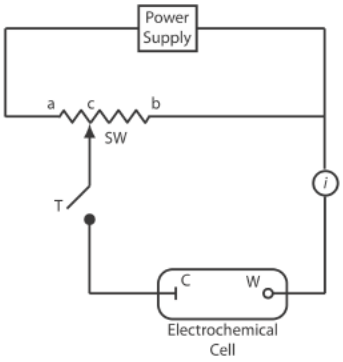


Figure 11.1.3 . Schematic diagram of a manual potentiometer: C is the counter electrode; W is the working electrode; SW is a slide-wire resistor; T is a tap key and *i* is an ammeter for measuring current.

GALVANOSTATS

A ***galvanostat***, a schematic diagram of which is shown in Figure 11.1.4 , allows us to control the current that flows through an electrochemical cell. The current from the power supply through the working electrode is

$$i = \frac{E_{PS}}{R + R_{cell}}$$

where E_{PS} is the potential of the power supply, R is the resistance of the resistor, and R_{cell} is the resistance of the electrochemical cell. If $R >> R_{cell}$, then the current between the auxiliary and working electrodes

$$i = \frac{E_{PS}}{R} \approx \text{constant}$$

maintains a constant value. To monitor the working electrode's potential, which changes as the composition of the electrochemical cell changes, we can include an optional reference electrode and a high-impedance potentiometer.

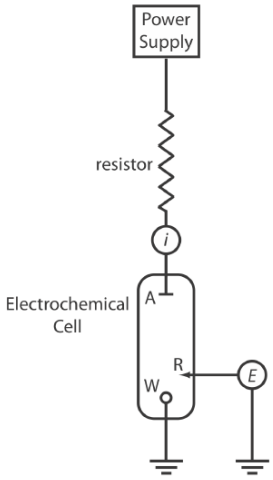


Figure 11.1.4 . Schematic diagram of a galvanostat: A is the auxiliary electrode; W is the working electrode; R is an optional reference electrode, *E* is a high-impedance potentiometer, and *i* is an ammeter. The working electrode and the optional reference electrode are connected to a ground.

POTENTIOSTATS

A ***potentiostat***, a schematic diagram of which is shown in Figure 11.1.5 , allows us to control the working electrode's potential. The potential of the working electrode is measured relative to a constant-potential reference electrode that is connected to the working electrode through a high-impedance potentiometer. To set the working electrode's potential we adjust the slide wire resistor that is connected to the auxiliary electrode. If the working electrode's potential begins to drift, we adjust the slide wire resistor to return the potential to its initial value. The current flowing between the auxiliary electrode and the working electrode is measured with an ammeter. Modern potentiostats include waveform generators that allow us to apply a time-dependent potential profile, such as a series of potential pulses, to the working electrode.

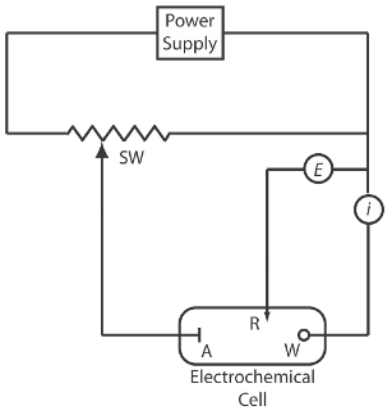


Figure 11.1.5 . Schematic diagram for a manual potentiostat: W is the working electrode; A is the auxiliary electrode; R is the reference electrode; SW is a slide-wire resistor, *E* is a high-impendance potentiometer; and *i* is an ammeter.

INTERFACIAL ELECTROCHEMICAL TECHNIQUES

Because interfacial electrochemistry is such a broad field, let's use Figure 11.1.6 to organize techniques by the experimental conditions we choose to use (Do we control the potential or the current? How do we change the applied potential or applied current? Do we stir the solution?) and the analytical signal we decide to measure (Current? Potential?).

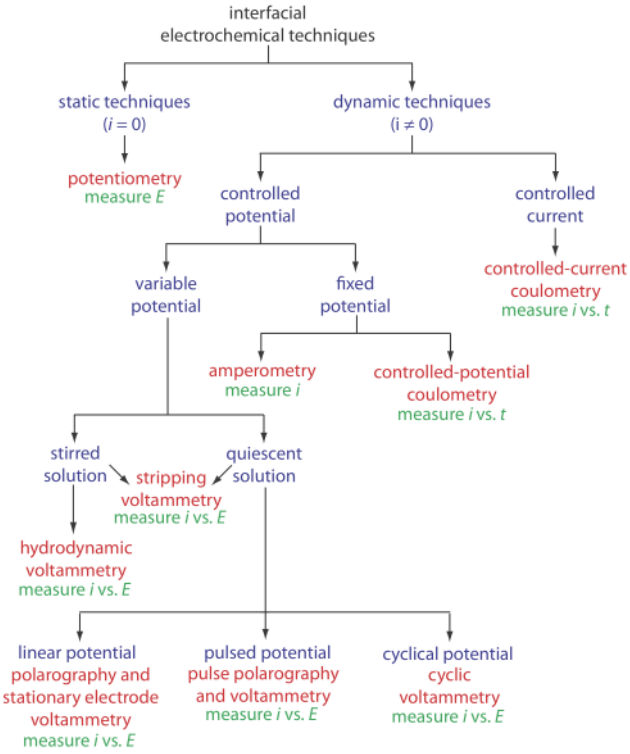


Figure 11.1.6 . Family tree that highlights the similarities and differences between a number of interfacial electrochemical techniques. The specific techniques are shown in red, the experimental conditions are shown in blue, and the analytical signals are shown in green.

At the first level, we divide interfacial electrochemical techniques into static techniques and dynamic techniques. In a static technique we do not allow current to pass through the electrochemical cell and, as a result, the concentrations of all species remain constant. Potentiometry, in which we measure the potential of an electrochemical cell under static conditions, is one of the most important quantitative electrochemical methods and is discussed in detail in Chapter 11.2.

Dynamic techniques, in which we allow current to flow and force a change in the concentration of species in the electrochemical cell, comprise the largest group of interfacial electrochemical techniques. Coulometry, in which we measure current as a function of time, is covered in Chapter 11.3. Amperometry and voltammetry, in which we measure current as a function of a fixed or variable potential, is the subject of Chapter 11.4.

11.2: POTENTIOMETRIC METHODS

In potentiometry we measure the potential of an electrochemical cell under static conditions. Because no current—or only a negligible current—flows through the electrochemical cell, its composition remains unchanged. For this reason, potentiometry is a useful quantitative method of analysis. The first quantitative potentiometric applications appeared soon after the formulation, in 1889, of the Nernst equation, which relates an electrochemical cell's potential to the concentration of electroactive species in the cell [Stork, J. T. *Anal. Chem.* **1993**, *65*, 344A–351A].

> For an on-line introduction to much of the material in this section, see Analytical Electrochemistry: Potentiometry by Erin Gross, Richard S. Kelly, and Donald M. Cannon, Jr., a resource that is part of the Analytical Sciences Digital Library.

Potentiometry initially was restricted to redox equilibria at metallic electrodes, which limited its application to a few ions. In 1906, Cremer discovered that the potential difference across a thin glass membrane is a function of pH when opposite sides of the membrane are in contact with solutions that have different concentrations of H_3O^+. This discovery led to the development of the glass pH electrode in 1909. Other types of membranes also yield useful potentials. For example, in 1937 Kolthoff and Sanders showed that a pellet of AgCl can be used to determine the concentration of Ag^+. Electrodes based on membrane potentials are called ion-selective electrodes, and their continued development extends potentiometry to a diverse array of analytes.

POTENTIOMETRIC MEASUREMENTS

As shown in Figure 11.1.3, we use a potentiometer to determine the difference between the potential of two electrodes. The potential of one electrode—the working or indicator electrode—responds to the analyte's activity and the other electrode—the counter or reference electrode—has a known, fixed potential. In this section we introduce the conventions for describing potentiometric electrochemical cells, and the relationship between the measured potential and the analyte's activity.

> In Chapter 6 we noted that a chemical reaction's equilibrium position is a function of the activities of the reactants and products, not their concentrations. To be correct, we should write the Nernst equation in terms of activities. So why didn't we use activities in Chapter 9 when we calculated redox titration curves? There are two reasons for that choice. First, concentrations are always easier to calculate than activities. Second, in a redox titration we determine the analyte's concentration from the titration's end point, not from the potential at the end point. The only reasons for calculating a titration curve is to evaluate its feasibility and to help us select a useful indicator. In most cases, the error we introduce by assuming that concentration and activity are identical is too small to be a significant concern.
>
> In potentiometry we cannot ignore the difference between activity and concentration. Later in this section we will consider how we can design a potentiometric method so that we can ignore the difference between activity and concentration. See Chapter 6.9 to review our earlier discussion of activity and concentration.

POTENTIOMETRIC ELECTROCHEMICAL CELLS

A schematic diagram of a typical potentiometric electrochemical cell is shown in Figure 11.2.1 . The electrochemical cell consists of two half-cells, each of which contains an electrode immersed in a solution of ions whose activities determine the electrode's potential. A ***salt bridge*** that contains an inert electrolyte, such as KCl, connects the two half-cells. The ends of the salt bridge are fixed with porous frits, which allow the electrolyte's ions to move freely between the half-cells and the salt bridge. This movement of ions in the salt bridge completes the electrical circuit.

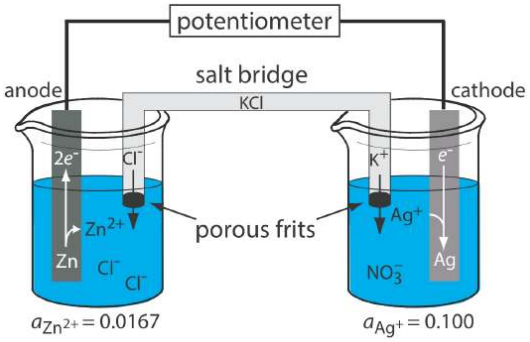


Figure 11.2.1 . Example of a potentiometric electrochemical cell. The activities of Zn^{2+} and Ag^+ are shown below the two half-cells.

By convention, we identify the electrode on the left as the ***anode*** and assign to it the oxidation reaction; thus

$$\mathrm{Zn}(s) \rightleftharpoons \mathrm{Zn}^{2+}(aq) + 2e^-$$

The electrode on the right is the ***cathode***, where the reduction reaction occurs.

$$\mathrm{Ag}^+(aq) + e^- \rightleftharpoons \mathrm{Ag}(s)$$

The potential of the electrochemical cell in Figure 11.2.1 is for the reaction

$$\mathrm{Zn}(s) + 2\mathrm{Ag}^+(aq) \rightleftharpoons 2\mathrm{Ag}(s) + \mathrm{Zn}^{2+}(\mathrm{aq})$$

We also define potentiometric electrochemical cells such that the cathode is the indicator electrode and the anode is the reference electrode.

> The reason for separating the electrodes is to prevent the oxidation reaction and the reduction reaction from occurring at one of the electrodes. For example, if we place a strip of Zn metal in a solution of $AgNO_3$, the reduction of Ag^+ to Ag occurs on the surface of the Zn at the same time as a potion of the Zn metal oxidizes to Zn^{2+}. Because the transfer of electrons from Zn to Ag^+ occurs at the electrode's surface, we can not pass them through the potentiometer.

SHORTHAND NOTATION FOR ELECTROCHEMICAL CELLS

Although Figure 11.2.1 provides a useful picture of an electrochemical cell, it is not a convenient way to represent it (Imagine having to draw a picture of each electrochemical cell you are using!). A more useful way to describe an electrochemical cell is a shorthand notation that uses symbols to identify different phases and that lists the composition of each phase. We use a vertical slash (|) to identify a boundary between two phases where a potential develops, and a comma (,) to separate species in the same phase or to identify a boundary between two phases where no potential develops. Shorthand cell notations begin with the anode and continue to the cathode. For example, we describe the electrochemical cell in Figure 11.2.1 using the following shorthand notation.

$$\mathrm{Zn}(s)|\mathrm{ZnCl}_2(aq, a_{\mathrm{Zn}^{2+}} = 0.0167)||\mathrm{AgNO}_3(aq, a_{\mathrm{Ag}^+} = 0.100)|\mathrm{Ag}(s)$$

The double vertical slash (||) represents the salt bridge, the contents of which we usually do not list. Note that a double vertical slash implies that there is a potential difference between the salt bridge and each half-cell.

✔ EXAMPLE 11.2.1

What are the anodic, the cathodic, and the overall reactions responsible for the potential of the electrochemical cell in Figure 11.2.2 ? Write the shorthand notation for the electrochemical cell.

Solution

The oxidation of Ag to Ag^+ occurs at the anode, which is the left half-cell. Because the solution contains a source of Cl^-, the anodic reaction is

$$\mathrm{Ag}(s) + \mathrm{Cl}^-(aq) \rightleftharpoons \mathrm{AgCl}(s) + e^-$$

The cathodic reaction, which is the right half-cell, is the reduction of Fe^{3+} to Fe^{2+}.

$$\mathrm{Fe}^{3+}(aq) + e^- \rightleftharpoons \mathrm{Fe}^{2+}(aq)$$

The overall cell reaction, therefore, is

$$Ag(s) + Fe^{3+}(aq) + Cl^{-}(aq) \rightleftharpoons AgCl(s) + Fe^{2+}(aq)$$

The electrochemical cell's shorthand notation is

$$Ag(s)|HCl(aq, a_{Cl^-} = 0.100), AgCl(sat'd)|$$
$$|FeCl_2(aq, a_{Fe^{2+}} = 0.0100), Fe^{3+}(aq, a_{Fe^{3+}} = 0.0500)|Pt(s)$$

Note that the Pt cathode is an inert electrode that carries electrons to the reduction half-reaction. The electrode itself does not undergo reduction.

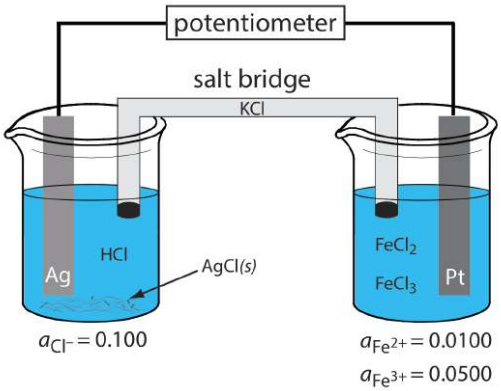


Figure 11.2.2 . Potentiometric electrochemical cell for Example 11.2.1 .

EXERCISE 11.2.1

Write the reactions occurring at the anode and the cathode for the potentiometric electrochemical cell with the following shorthand notation.

$$Pt(s) \mid H_2(g), H^+(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

Answer

The oxidation of H_2 to H^+ occurs at the anode

$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$

and the reduction of Cu^{2+} to Cu occurs at the cathode.

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

The overall cell reaction, therefore, is

$$Cu^{2+}(aq) + H_2(g) \rightleftharpoons 2H^+(aq) + Cu(s)$$

POTENTIAL AND ACTIVITY—THE NERNST EQUATION

The potential of a potentiometric electrochemical cell is

$$E_{cell} = E_{cathode} - E_{anode} \tag{11.2.1}$$

where $E_{cathode}$ and E_{anode} are reduction potentials for the redox reactions at the cathode and the anode, respectively. Each reduction potential is given by the Nernst equation

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

where E^o is the standard-state reduction potential, R is the gas constant, T is the temperature in Kelvins, n is the number of electrons in the redox reaction, F is Faraday's constant, and Q is the reaction quotient. At a temperature of 298 K (25°C) the Nernst equation is

$$E = E^\circ - \frac{0.05916}{n} \log Q \tag{11.2.2}$$

where E is in volts.

Using Equation 11.2.2, the potential of the anode and cathode in Figure 11.2.1 are

$$E_{\text{anode}} = E^\circ_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.05916}{2}\log\frac{1}{a_{\text{Zn}^{2+}}}$$

$$E_{\text{anode}} = E^\circ_{\text{Ag}^{+}/\text{Ag}} - \frac{0.05916}{1}\log\frac{1}{a_{\text{Ag}^{+}}}$$

Even though an oxidation reaction is taking place at the anode, we define the anode's potential in terms of the corresponding reduction reaction and the standard-state reduction potential. See Chapter 6.4 for a review of using the Nernst equation in calculations.

Substituting E_{cathode} and E_{anode} into Equation 11.2.1, along with the activities of Zn^{2+} and Ag^{+} and the standard-state reduction potentials, gives E_{cell} as

$$E_{\text{cell}} = \left(E^\circ_{\text{Ag}^{+}/\text{Ag}} - \frac{0.05916}{1}\log\frac{1}{a_{\text{Ag}^{+}}}\right) - \left(E^\circ_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.05916}{2}\log\frac{1}{a_{\text{Zn}^{2+}}}\right)$$

$$E_{\text{cell}} = \left(0.7996 - \frac{0.05916}{1}\log\frac{1}{0.100}\right) - \left(-0.7618 - \frac{0.05916}{2}\log\frac{1}{0.0167}\right) = 1.555\ \text{V}$$

You will find values for the standard-state reduction potentials in Appendix 13.

EXAMPLE 11.2.2

What is the potential of the electrochemical cell shown in Example 11.2.1 ?

Solution

Substituting E_{cathode} and E_{anode} into Equation 11.2.1, along with the concentrations of Fe^{3+}, Fe^{2+}, and Cl^{-} and the standard-state reduction potentials gives

$$E_{\text{cell}} = \left(E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - \frac{0.05916}{1}\log\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}}\right) - \left(E^\circ_{\text{AgCl/Ag}} - \frac{0.05916}{1}\log a_{\text{Cl}^{-}}\right)$$

$$E_{\text{cell}} = \left(0.771 - \frac{0.05916}{1}\log\frac{0.0100}{0.0500}\right) - \left(0.2223 - \frac{0.05916}{1}\log(0.100)\right) = 0.531\ \text{V}$$

EXERCISE 11.2.2

What is the potential for the electrochemical cell in Exercise 11.2.1 if the activity of H^{+} in the anodic half-cell is 0.100, the fugacity of H_2 in the anodic half-cell is 0.500, and the activity of Cu^{2+} in the cathodic half-cell is 0.0500? Fugacity, f, is the equivalent term for the activity of a gas.

Answer

Making appropriate substitutions into Equation 11.2.1 and solving for E_{cell} gives its value as

$$E_{\text{cell}} = \left(E^\circ_{\text{Cu}^{2+}/\text{Cu}} - \frac{0.05916}{2}\log\frac{1}{a_{\text{Cu}^{2+}}}\right) - \left(E^\circ_{\text{H}^{+}/\text{H}_2} - \frac{0.05916}{2}\log\frac{f_{\text{H}_2}}{a^2_{\text{H}^{+}}}\right)$$

$$E_{\text{cell}} = \left(0.3419 - \frac{0.05916}{2}\log\frac{1}{0.0500}\right) - \left(0.0000 - \frac{0.05916}{2}\log\frac{0.500}{(0.100)^2}\right) = 0.3537\ \text{V}$$

In potentiometry, we assign the reference electrode to the anodic half-cell and assign the indicator electrode to the cathodic half-cell. Thus, if the potential of the cell in Figure 11.2.1 is +1.50 V and the activity of Zn^{2+} is 0.0167, then we can solve the following equation for $a_{\text{Ag}^{+}}$

$$1.50\ \text{V} = \left(0.7996 - \frac{0.05916}{1}\log\frac{1}{a_{\text{Ag}^{+}}}\right) - \left(-0.7618 - \frac{0.05916}{2}\log\frac{1}{0.0167}\right)$$

obtaining an activity of 0.0118.

EXAMPLE 11.2.3

What is the activity of Fe^{3+} in an electrochemical cell similar to that in Example 11.2.1 if the activity of Cl^- in the left-hand cell is 1.0, the activity of Fe^{2+} in the right-hand cell is 0.015, and E_{cell} is +0.546 V?

Solution

Making appropriate substitutions into Equation 11.2.1

$$0.546 = \left(0.771 - \frac{0.05916}{1}\log\frac{0.0100}{a_{Fe^{3+}}}\right) - \left(0.2223 - \frac{0.05916}{1}\log(1.0)\right)$$

and solving for $a_{Fe^{3+}}$ gives its activity as 0.0135.

? EXERCISE 11.2.3

What is the activity of Cu^{2+} in the electrochemical cell in Exercise 11.2.1 if the activity of H^+ in the anodic half-cell is 1.00 with a fugacity of 1.00 for H_2, and an E_{cell} of +0.257 V?

Answer

Making appropriate substitutions into Equation 11.2.1

$$0.257\ \text{V} = \left(0.3419 - \frac{0.05916}{2}\log\frac{1}{a_{Cu^{2+}}}\right) - \left(0.0000 - \frac{0.05916}{2}\log\frac{1.00}{(1.00)^2}\right)$$

and solving for $a_{Cu^{2+}}$ gives its activity as 1.35×10^{-3}.

Despite the apparent ease of determining an analyte's activity using the Nernst equation, there are several problems with this approach. One problem is that standard-state potentials are temperature-dependent and the values in reference tables usually are for a temperature of 25°C. We can overcome this problem by maintaining the electrochemical cell at 25°C or by measuring the standard-state potential at the desired temperature.

Another problem is that a standard-sate reduction potential may have a significant matrix effect. For example, the standard-state reduction potential for the Fe^{3+}/Fe^{2+} redox couple is +0.735 V in 1 M $HClO_4$, +0.70 V in 1 M HCl, and +0.53 V in 10 M HCl. The difference in potential for equimolar solutions of HCl and $HClO_4$ is the result of a difference in the activity coefficients for Fe^{3+} and Fe^{2+} in these two media. The shift toward a more negative potential with an increase in the concentration of HCl is the result of chloride's ability to form a stronger complex with Fe^{3+} than with Fe^{2+}. We can minimize this problem by replacing the standard-state potential with a matrix-dependent formal potential. Most tables of standard-state potentials, including those in Appendix 13, include selected formal potentials.

Finally, a more serious problem is the presence of additional potentials in the electrochemical cell not included in Equation 11.2.1. In writing the shorthand notation for an electrochemical cell we use a double slash (||) to indicate the salt bridge, suggesting a potential exists at the interface between each end of the salt bridge and the solution in which it is immersed. The origin of this potential is discussed in the following section.

JUNCTION POTENTIALS

A ***junction potential*** develops at the interface between two ionic solution if there is a difference in the concentration and mobility of the ions. Consider, for example, a porous membrane that separations a solution of 0.1 M HCl from a solution of 0.01 M HCl (Figure 11.2.3 a). Because the concentration of HCl on the membrane's left side is greater than that on the right side of the membrane, H^+ and Cl^- will diffuse in the direction of the arrows. The mobility of H^+, however, is greater than that for Cl^-, as shown by the difference in the lengths of their respective arrows. Because of this difference in mobility, the solution on the right side of the membrane develops an excess concentration of H^+ and a positive charge (Figure 11.2.3 b). Simultaneously, the solution on the membrane's left side develops a negative charge because there is an excess concentration of Cl^-. We call this difference in potential across the membrane a junction potential and represent it as E_j.

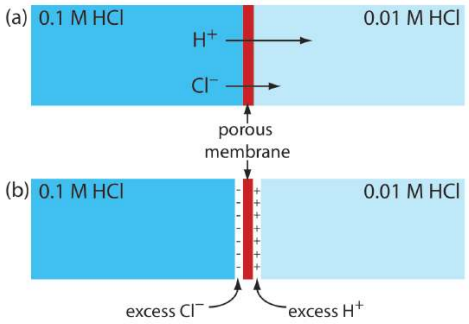


Figure 11.2.3 . Origin of the junction potential between a solution of 0.1 M HCl and a solution of 0.01 M HCl.

The magnitude of the junction potential depends upon the difference in the concentration of ions on the two sides of the interface, and may be as large as 30–40 mV. For example, a junction potential of 33.09 mV has been measured at the interface between solutions of 0.1 M HCl and 0.1 M NaCl [Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*, Wiley-Interscience: New York, 1974, p. 22]. A salt bridge's junction potential is minimized by using a salt, such as KCl, for which the mobilities of the cation and anion are approximately equal. We also can minimize the junction potential by incorporating a high concentration of the salt in the salt bridge. For this reason salt bridges frequently are constructed using solutions that are saturated with KCl. Nevertheless, a small junction potential, generally of unknown magnitude, is always present.

When we measure the potential of an electrochemical cell, the junction potential also contributes to E_{cell}; thus, we rewrite Equation 11.2.1 as

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} + E_j$$

to include its contribution. If we do not know the junction potential's actual value—which is the usual situation—then we cannot directly calculate the analyte's concentration using the Nernst equation. Quantitative analytical work is possible, however, if we use one of the standardization methods—external standards, the method of standard additions, or internal standards—discussed in Chapter 5.3.

REFERENCE ELECTRODES

In a potentiometric electrochemical cell one of the two half-cells provides a fixed reference potential and the potential of the other half-cell responds the analyte's concentration. By convention, the reference electrode is the anode; thus, the short hand notation for a potentiometric electrochemical cell is

reference electrode || indicator electrode

and the cell potential is

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_j$$

The ideal reference electrode provides a stable, known potential so that we can attribute any change in E_{cell} to the analyte's effect on the indicator electrode's potential. In addition, it should be easy to make and to use the reference electrode. Three common reference electrodes are discussed in this section.

STANDARD HYDROGEN ELECTRODE

Although we rarely use the ***standard hydrogen electrode*** (SHE) for routine analytical work, it is the reference electrode used to establish standard-state potentials for other half-reactions. The SHE consists of a Pt electrode immersed in a solution in which the activity of hydrogen ion is 1.00 and in which the fugacity of $H_2(g)$ is 1.00 (Figure 11.2.4). A conventional salt bridge connects the SHE to the indicator half-cell. The short hand notation for the standard hydrogen electrode is

$$\text{Pt}(s),\ \text{H}_2\,(g, f_{\text{H}_2} = 1.00)\ |\ \text{H}^+\,(aq, a_{\text{H}^+} = 1.00)\ \|$$

and the standard-state potential for the reaction

$$\text{H}^+(aq) + e^- = \frac{1}{2}\text{H}_2(g)$$

is, by definition, 0.00 V at all temperatures. Despite its importance as the fundamental reference electrode against which we measure all other potentials, the SHE is rarely used because it is difficult to prepare and inconvenient to use.

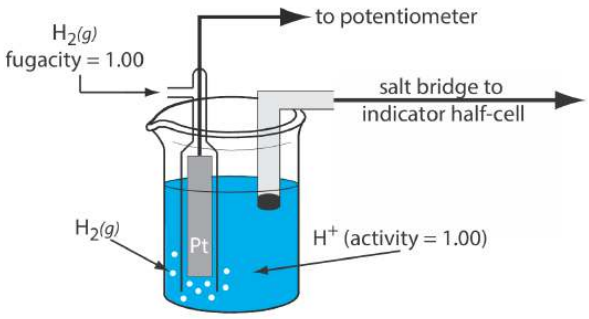


Figure 11.2.4 . Schematic diagram showing the standard hydrogen electrode.

CALOMEL ELECTRODES

A calomel reference electrode is based on the following redox couple between Hg_2Cl_2 and Hg (calomel is the common name for Hg_2Cl_2)

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$$

for which the potential is

$$E = E^\circ_{Hg_2Cl_2/Hg} - \frac{0.05916}{2}\log\left(a_{Cl^-}\right)^2 = +0.2682V - \frac{0.05916}{2}\log\left(a_{Cl^-}\right)^2$$

The potential of a calomel electrode, therefore, depends on the activity of Cl^- in equilibrium with Hg and Hg_2Cl_2.

As shown in Figure 11.2.5 , in a ***saturated calomel electrode*** (SCE) the concentration of Cl^- is determined by the solubility of KCl. The electrode consists of an inner tube packed with a paste of Hg, Hg_2Cl_2, and KCl, situated within a second tube that contains a saturated solution of KCl. A small hole connects the two tubes and a porous wick serves as a salt bridge to the solution in which the SCE is immersed. A stopper in the outer tube provides an opening for adding addition saturated KCl. The short hand notation for this cell is

$$Hg(l)|Hg_2Cl_2(s), KCl(aq,\ \text{sat'd}\ )\|$$

Because the concentration of Cl^- is fixed by the solubility of KCl, the potential of an SCE remains constant even if we lose some of the inner solution to evaporation. A significant disadvantage of the SCE is that the solubility of KCl is sensitive to a change in temperature. At higher temperatures the solubility of KCl increases and the electrode's potential decreases. For example, the potential of the SCE is +0.2444 V at 25ºC and +0.2376 V at 35ºC. The potential of a calomel electrode that contains an unsaturated solution of KCl is less dependent on the temperature, but its potential changes if the concentration, and thus the activity of Cl^-, increases due to evaporation.

> For example, the potential of a calomel electrode is +0.280 V when the concentration of KCl is 1.00 M and +0.336 V when the concentration of KCl is 0.100 M. If the activity of Cl^- is 1.00, the potential is +0.2682 V.

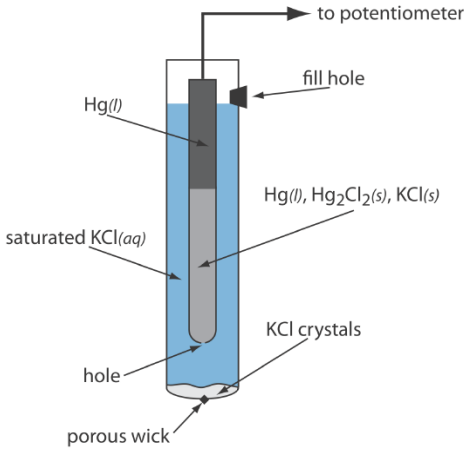


Figure 11.2.5 . Schematic diagram showing the saturated calomel electrode.

SILVER/SILVER CHLORIDE ELECTRODES

Another common reference electrode is the ***silver/silver chloride electrode***, which is based on the reduction of AgCl to Ag.

$$\mathrm{AgCl}(s) + e^- \rightleftharpoons \mathrm{Ag}(s) + \mathrm{Cl}^-(aq)$$

As is the case for the calomel electrode, the activity of Cl^- determines the potential of the Ag/AgCl electrode; thus

$$E = E^\circ_{\mathrm{AgCl/Ag}} - 0.05916 \log a_{\mathrm{Cl}^-} = 0.2223 \text{ V} - 0.05916 \log a_{\mathrm{Cl}^-}$$

When prepared using a saturated solution of KCl, the electrode's potential is +0.197 V at 25°C. Another common Ag/AgCl electrode uses a solution of 3.5 M KCl and has a potential of +0.205 V at 25°C. As you might expect, the potential of a Ag/AgCl electrode using a saturated solution of KCl is more sensitive to a change in temperature than an electrode that uses an unsaturated solution of KCl.

A typical Ag/AgCl electrode is shown in Figure 11.2.6 and consists of a silver wire, the end of which is coated with a thin film of AgCl, immersed in a solution that contains the desired concentration of KCl. A porous plug serves as the salt bridge. The electrode's short hand notation is

$$\mathrm{Ag}(s)|\,\mathrm{Ag\,Cl}(s), \mathrm{KCl}\,(aq, a_{\mathrm{Cl}^-} = x)\,\|$$

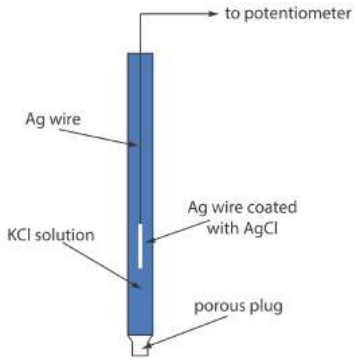


Figure 11.2.6 . Schematic diagram showing a Ag/AgCl electrode. Because the electrode does not contain solid KCl, this is an example of an unsaturated Ag/AgCl electrode.

CONVERTING POTENTIALS BETWEEN REFERENCE ELECTRODES

The standard state reduction potentials in most tables are reported relative to the standard hydrogen electrode's potential of +0.00 V. Because we rarely use the SHE as a reference electrode, we need to convert an indicator electrode's potential to its equivalent value when using a different reference electrode. As shown in the following example, this is easy to do.

✔ EXAMPLE 11.2.4

The potential for an Fe^{3+}/Fe^{2+} half-cell is +0.750 V relative to the standard hydrogen electrode. What is its potential if we use a saturated calomel electrode or a saturated silver/silver chloride electrode?

Solution

When we use a standard hydrogen electrode the potential of the electrochemical cell is

$$E_{\text{cell}} = E_{\mathrm{Fe^{3+}/Fe^{2+}}} - E_{\text{SHE}} = 0.750 \text{ V} - 0.000 \text{ V} = 0.750 \text{ V}$$

We can use the same equation to calculate the potential if we use a saturated calomel electrode

$$E_{\text{cell}} = E_{\mathrm{Fe^{3+}/Fe^{2+}}} - E_{\text{SHE}} = 0.750 \text{ V} - 0.2444 \text{ V} = 0.506 \text{ V}$$

or a saturated silver/silver chloride electrode

$$E_{\text{cell}} = E_{\mathrm{Fe^{3+}/Fe^{2+}}} - E_{\text{SHE}} = 0.750 \text{ V} - 0.197 \text{ V} = 0.553 \text{ V}$$

Figure 11.2.7 provides a pictorial representation of the relationship between these different potentials.

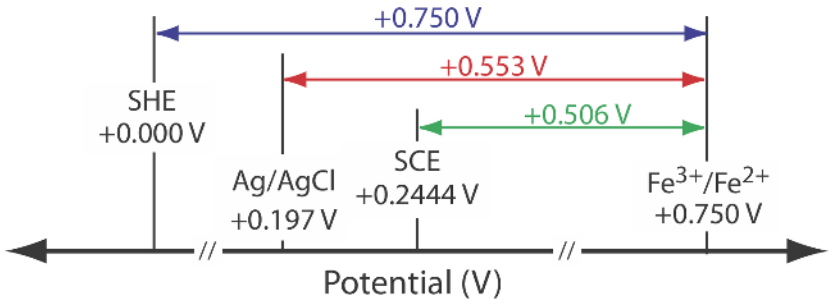


Figure 11.2.7 . Relationship between the potential of an Fe^{3+}/Fe^{2+} half-cell relative to the reference electrodes in Example 11.2.4 . The potential relative to a standard hydrogen electrode is shown in blue, the potential relative to a saturated silver/silver chloride electrode is shown in red, and the potential relative to a saturated calomel electrode is shown in green.

? EXERCISE 11.2.4

The potential of a UO_2^+/U^{4+} half-cell is –0.0190 V relative to a saturated calomel electrode. What is its potential when using a saturated silver/silver chloride electrode or a standard hydrogen electrode?

Answer

When using a saturated calomel electrode, the potential of the electro- chemical cell is

$$E_{\text{cell}} = E_{UO_2^+/U^{4+}} - E_{\text{SCE}}$$

Substituting in known values

$$-0.0190\ \text{V} = E_{UO_2^+/U^{4+}} - 0.2444\ \text{V}$$

and solving for $E_{UO_2^+/U^{4+}}$ gives its value as +0.2254 V. The potential relative to the Ag/AgCl electrode is

$$E_{\text{cell}} = E_{UO_2^+/U^{4+}} - E_{\text{Ag/AgCl}} = 0.2254\ \text{V} - 0.197\ \text{V} = 0.028\ \text{V}$$

and the potential relative to the standard hydrogen electrode is

$$E_{\text{cell}} = E_{UO_2^+/U^{4+}} - E_{\text{SHE}} = 0.2254\ \text{V} - 0.000\ \text{V} = 0.2254\ \text{V}$$

METALLIC INDICATOR ELECTRODES

In potentiometry, the potential of the indicator electrode is proportional to the analyte's activity. Two classes of indicator electrodes are used to make potentiometric measurements: metallic electrodes, which are the subject of this section, and ion-selective electrodes, which are covered in the next section.

ELECTRODES OF THE FIRST KIND

If we place a copper electrode in a solution that contains Cu^{2+}, the electrode's potential due to the reaction

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

is determined by the activity of Cu^{2+}.

$$E = E^\circ_{Cu^{2+}/Cu} - \frac{0.05916}{2}\log\frac{1}{a_{Cu^{2+}}} = +0.3419\text{V} - \frac{0.05916}{2}\log\frac{1}{a_{Cu^{2+}}}$$

If copper is the indicator electrode in a potentiometric electrochemical cell that also includes a saturated calomel reference electrode

$$\text{SCE}\|Cu^{2+}\,(aq, a_{Cu^{2+}} = x)\,|Cu(s)$$

then we can use the cell potential to determine an unknown activity of Cu^{2+} in the indicator electrode's half-cell

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{SCE}} + E_j = +0.3419\text{V} - \frac{0.05916}{2}\log\frac{1}{a_{Cu^{2+}}} - 0.2224\text{V} + E_j$$

An indicator electrode in which the metal is in contact with a solution containing its ion is called an ***electrode of the first kind***. In general, if a metal, M, is in a solution of M^{n+}, the cell potential is

$$E_{cell} = K - \frac{0.05916}{n} \log \frac{1}{a_{M^{n+}}} = K + \frac{0.05916}{n} \log a_{M^{n+}}$$

where K is a constant that includes the standard-state potential for the M^{n+}/M redox couple, the potential of the reference electrode, and the junction potential.

> Note that including E_j in the constant K means we do not need to know the junction potential's actual value; however, the junction potential must remain constant if K is to maintain a constant value.

For a variety of reasons—including the slow kinetics of electron transfer at the metal–solution interface, the formation of metal oxides on the electrode's surface, and interfering reactions—electrodes of the first kind are limited to the following metals: Ag, Bi, Cd, Cu, Hg, Pb, Sn, Tl, and Zn.

> Many of these electrodes, such as Zn, cannot be used in acidic solutions because they are easily oxidized by H^+.
>
> $$Zn(s) + 2H^+(aq) \rightleftharpoons H_2(g) + Zn^{2+}(aq)$$

ELECTRODES OF THE SECOND KIND

The potential of an electrode of the first kind responds to the activity of M^{n+}. We also can use this electrode to determine the activity of another species if it is in equilibrium with M^{n+}. For example, the potential of a Ag electrode in a solution of Ag^+ is

$$E = 0.7996 V + 0.05916 \log a_{Ag^+} \tag{11.2.3}$$

If we saturate the indicator electrode's half-cell with AgI, the solubility reaction

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

determines the concentration of Ag^+; thus

$$a_{Ag^+} = \frac{K_{sp,AgI}}{a_{I^-}} \tag{11.2.4}$$

where $K_{sp,AgI}$ is the solubility product for AgI. Substituting Equation 11.2.4 into Equation 11.2.3

$$E = 0.7996 \text{ V} + 0.05916 \log \frac{K_{sp,\ AgI}}{a_{I^-}}$$

shows that the potential of the silver electrode is a function of the activity of I^-. If we incorporate this electrode into a potentiometric electrochemical cell with a saturated calomel electrode

$$SCE \| AgI(s),\ I^-\ (aq, a_{I^-} = x)\ | Ag(s)$$

then the cell potential is

$$E_{cell} = K - 0.05916 \log a_{I^-}$$

where K is a constant that includes the standard-state potential for the Ag^+/Ag redox couple, the solubility product for AgI, the reference electrode's potential, and the junction potential.

If an electrode of the first kind responds to the activity of an ion in equilibrium with M^{n+}, we call it an ***electrode of the second kind***. Two common electrodes of the second kind are the calomel and the silver/silver chloride reference electrodes.

> In an electrode of the second kind we link together a redox reaction and another reaction, such as a solubility reaction. You might wonder if we can link together more than two reactions. The short answer is yes. An electrode of the third kind, for example, links together a redox reaction and two other reactions. Such electrodes are less common and we will not consider them in this text.

REDOX ELECTRODES

An electrode of the first kind or second kind develops a potential as the result of a redox reaction that involves the metallic electrode. An electrode also can serve as a source of electrons or as a sink for electrons in an unrelated redox reaction, in which case we call it a ***redox electrode.*** The Pt cathode in Figure 11.2.2 and Example 11.2.1 is a redox electrode because its potential is determined by the activity of Fe^{2+}

and Fe^{3+} in the indicator half-cell. Note that a redox electrode's potential often responds to the activity of more than one ion, which limits its usefulness for direct potentiometry.

MEMBRANE ELECTRODES

If metals were the only useful materials for constructing indicator electrodes, then there would be few useful applications of potentiometry. In 1906, Cremer discovered that the potential difference across a thin glass membrane is a function of pH when opposite sides of the membrane are in contact with solutions that have different concentrations of H_3O^+. The existence of this ***membrane potential*** led to the development of a whole new class of indicator electrodes, which we call ***ion-selective electrodes*** (ISEs). In addition to the glass pH electrode, ion-selective electrodes are available for a wide range of ions. It also is possible to construct a membrane electrode for a neutral analyte by using a chemical reaction to generate an ion that is monitored with an ion-selective electrode. The development of new membrane electrodes continues to be an active area of research.

MEMBRANE POTENTIALS

Figure 11.2.8 shows a typical potentiometric electrochemical cell equipped with an ion-selective electrode. The short hand notation for this cell is

$$\text{ref (sample)} \; \| [\text{A}]_{\text{samp}} \; (aq, a_{\text{A}} = x) \, | [\text{A}]_{\text{int}} \; (aq, a_{\text{A}} = y) \| \; \text{ref (internal)}$$

where the ion-selective membrane is represented by the vertical slash that separates the two solutions that contain analyte: the sample solution and the ion-selective electrode's internal solution. The potential of this electrochemical cell includes the potential of each reference electrode, a junction potential, and the membrane's potential

$$E_{\text{cell}} = E_{\text{ref(int)}} - E_{\text{ref(samp)}} + E_{\text{mem}} + E_j \tag{11.2.5}$$

where E_{mem} is the potential across the membrane and The notations ref(sample) and ref(internal) represent a reference electrode immersed in the sample and a reference electrode immersed in the ISE's internal solution. Because the junction potential and the potential of the two reference electrodes are constant, any change in E_{cell} reflects a change in the membrane's potential.

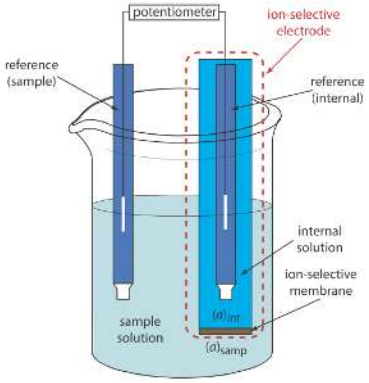


Figure 11.2.8 . Schematic diagram that shows a typical potentiometric cell with an ion-selective electrode. The ion-selective electrode's membrane separates the sample, which contains the analyte at an activity of $(a_A)_{\text{samp}}$, from an internal solution that contains the analyte with an activity of $(a_A)_{\text{int}}$.

The analyte's interaction with the membrane generates a membrane potential if there is a difference in its activity on the membrane's two sides. Current is carried through the membrane by the movement of either the analyte or an ion already present in the membrane's matrix. The membrane potential is given by the following Nernst-like equation

$$E_{\text{mem}} = E_{\text{asym}} - \frac{RT}{zF} \ln \frac{(a_A)_{\text{int}}}{(a_A)_{\text{samp}}} \tag{11.2.6}$$

where $(a_A)_{\text{samp}}$ is the analyte's activity in the sample, $(a_A)_{\text{int}}$ is the analyte's activity in the ion-selective electrode's internal solution, and z is the analyte's charge. Ideally, E_{mem} is zero when $(a_A)_{\text{int}} = (a_A)_{\text{samp}}$. The term E_{asym}, which is an ***asymmetry potential***, accounts for the fact that E_{mem} usually is not zero under these conditions.

> For now we simply note that a difference in the analyte's activity results in a membrane potential. As we consider different types of ion-selective electrodes, we will explore more specifically the source of the membrane potential.

Substituting Equation 11.2.6 into Equation 11.2.5, assuming a temperature of 25°C, and rearranging gives

$$E_{cell} = K + \frac{0.05916}{z}\log\left(a_A\right)_{samp} \tag{11.2.7}$$

where K is a constant that includes the potentials of the two reference electrodes, the junction potentials, the asymmetry potential, and the analyte's activity in the internal solution. Equation 11.2.7 is a general equation and applies to all types of ion-selective electrodes.

SELECTIVITY OF MEMBRANES

A membrane potential results from a chemical interaction between the analyte and active sites on the membrane's surface. Because the signal depends on a chemical process, most membranes are not selective toward a single analyte. Instead, the membrane potential is proportional to the concentration of each ion that interacts with the membrane's active sites. We can rewrite Equation 11.2.7 to include the contribution to the potential of an interferent, I

$$E_{cell} = K + \frac{0.05916}{z_A}\log\left\{a_A + K_{A,I}(a_I)^{z_A/z_I}\right\}$$

where z_A and z_I are the charges of the analyte and the interferent, and $K_{A,I}$ is a selectivity coefficient that accounts for the relative response of the interferent. The selectivity coefficient is defined as

$$K_{A,I} = \frac{(a_A)_e}{(a_I)_e^{z_A/z_I}} \tag{11.2.8}$$

where $(a_A)_e$ and $(a_I)_e$ are the activities of analyte and the interferent that yield identical cell potentials. When the selectivity coefficient is 1.00, the membrane responds equally to the analyte and the interferent. A membrane shows good selectivity for the analyte when $K_{A,I}$ is significantly less than 1.00.

Selectivity coefficients for most commercially available ion-selective electrodes are provided by the manufacturer. If the selectivity coefficient is not known, it is easy to determine its value experimentally by preparing a series of solutions, each of which contains the same activity of interferent, $(a_I)_{add}$, but a different activity of analyte. As shown in Figure 11.2.9 , a plot of cell potential versus the log of the analyte's activity has two distinct linear regions. When the analyte's activity is significantly larger than $K_{A,I} \times (a_I)_{add}$, the potential is a linear function of $\log(a_A)$, as given by Equation 11.2.7. If $K_{A,I} \times (a_I)_{add}$ is significantly larger than the analyte's activity, however, the cell's potential remains constant. The activity of analyte and interferent at the intersection of these two linear regions is used to calculate $K_{A,I}$.

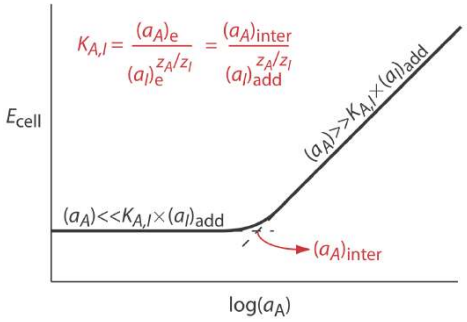


Figure 11.2.9 . Diagram showing the experimental determination of an ion-selective electrode's selectivity for an analyte. The activity of analyte that corresponds to the intersection of the two linear portions of the curve, $(a_A)_{inter}$, produces a cell potential identical to that of the interferent. The equation for the selectivity coefficient, $K_{A,I}$, is shown in red.

✔ EXAMPLE 11.2.5

Sokalski and co-workers described a method for preparing ion-selective electrodes with significantly improved selectivities [Sokalski, T.; Ceresa, A.; Zwicki, T.; Pretsch, E. *J. Am. Chem. Soc.* **1997**, *119*, 11347–11348]. For example, a conventional Pb^{2+} ISE has a $\log K_{Pb^{2+}/Mg^{2+}}$ of –3.6. If the potential for a solution in which the activity of Pb^{2+} is 4.1×10^{-12} is identical to that for a solution in which the activity of Mg^{2+} is 0.01025, what is the value of $\log K_{Pb^{2+}/Mg^{2+}}$ for their ISE?

Solution

Making appropriate substitutions into Equation 11.2.8, we find that

$$K_{Pb^{2+}/Mg^{2+}} = \frac{(a_{Pb^{2+}})_e}{(a_{Mg^{2+}})_e^{z_{Pb^{2+}}/z_{Mg^{2+}}}} = \frac{4.1 \times 10^{-12}}{(0.01025)^{+2/+2}} = 4.0 \times 10^{-10}$$

The value of $\log K_{Pb^{2+}/Mg^{2+}}$, therefore, is –9.40.

EXERCISE 11.2.5

A ion-selective electrode for NO_2^- has log$K_{A,I}$ values of –3.1 for F^-, –4.1 for SO_4^{2-}, –1.2 for I^-, and –3.3 for NO_3^-. Which ion is the most serious interferent and for what activity of this interferent is the potential equivalent to a solution in which the activity of NO_2^- is 2.75×10^{-4}?

Answer

The larger the value of $K_{A,I}$ the more serious the interference. Larger values for $K_{A,I}$ correspond to more positive (less negative) values for log$K_{A,I}$; thus, I^-, with a $K_{A,I}$ of 6.3×10^{-2}, is the most serious of these interferents. To find the activity of I^- that gives a potential equivalent to a NO_2^- activity of 2.75×10^{-4}, we note that

$$a_{NO_2^-} = K_{A,I} \times a_{I^-}$$

Making appropriate substitutions

$$2.75 \times 10^{-4} = (6.3 \times 10^{-2}) \times a_{I^-}$$

and solving for a_{I^-} gives its activity as 4.4×10^{-3}.

GLASS ION-SELECTIVE ELECTRODES

The first commercial ***glass electrodes*** were manufactured using Corning 015, a glass with a composition that is approximately 22% Na_2O, 6% CaO, and 72% SiO_2. When immersed in an aqueous solution for several hours, the outer approximately 10 nm of the membrane's surface becomes hydrated, resulting in the formation of negatively charged sites, —SiO^-. Sodium ions, Na^+, serve as counter ions. Because H^+ binds more strongly to —SiO^- than does Na^+, they displace the sodium ions

$$H^+ + -SiO^-Na^+ \rightleftharpoons -SiO^-H^+ + Na^+$$

explaining the membrane's selectivity for H^+. The transport of charge across the membrane is carried by the Na^+ ions. The potential of a glass electrode using Corning 015 obeys the equation

$$E_{cell} = K + 0.05916 \log a_{H^+} \tag{11.2.9}$$

over a pH range of approximately 0.5 to 9. At more basic pH values the glass membrane is more responsive to other cations, such as Na^+ and K^+.

EXAMPLE 11.2.6

For a Corning 015 glass membrane, the selectivity coefficient K_{H^+/Na^+} is $\approx 10^{-11}$. What is the expected error if we measure the pH of a solution in which the activity of H^+ is 2×10^{-13} and the activity of Na^+ is 0.05?

Solution

A solution in which the actual activity of H^+, $(a_{H^+})_{act}$, is 2×10^{-13} has a pH of 12.7. Because the electrode responds to both H^+ and Na^+, the apparent activity of H^+, $(a_{H^+})_{app}$, is

$$(a_{H^+})_{app} = (a_{H^+})_{act} + (K_{H^+/Na^+} \times a_{Na^+}) = 2 \times 10^{-13} + (10^{-11} \times 0.05) = 7 \times 10^{-13}$$

The apparent activity of H^+ is equivalent to a pH of 12.2, an error of –0.5 pH units.

Replacing Na_2O and CaO with Li_2O and BaO extends the useful pH range of glass membrane electrodes to pH levels greater than 12.

Glass membrane pH electrodes often are available in a combination form that includes both the indicator electrode and the reference electrode. The use of a single electrode greatly simplifies the measurement of pH. An example of a typical combination electrode is shown in Figure 11.2.10 .

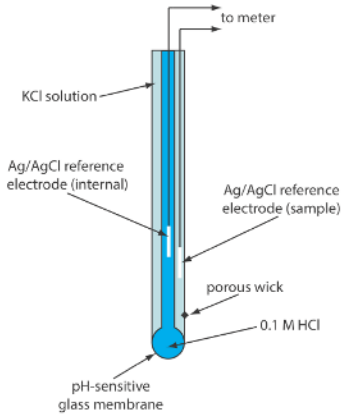


Figure 11.2.10 . Schematic diagram showing a combination glass electrode for measuring pH. The indicator electrode consists of a pH-sensitive glass membrane and an internal Ag/AgCl reference electrode in a solution of 0.1 M HCl. The sample's reference electrode is a Ag/AgCl electrode in a solution of KCl (which may be saturated with KCl or contain a fixed concentration of KCl). A porous wick serves as a salt bridge between the sample and its reference electrode.

The observation that the Corning 015 glass membrane responds to ions other than H^+ (see Example 11.2.6) led to the development of glass membranes with a greater selectivity for other cations. For example, a glass membrane with a composition of 11% Na_2O, 18% Al_2O_3, and 71% SiO_2 is used as an ion-selective electrode for Na^+. Other glass ion-selective electrodes have been developed for the analysis of Li^+, K^+, Rb^+, Cs^+, NH_4^+, Ag^+, and Tl^+. Table 11.2.1 provides several examples.

Table 11.2.1 . Representative Examples of Glass Membrane Ion-Selective Electrodes for Analytes Other Than H^+

analyte	membrane composition	selectivity coefficients
Na^+	11% Na_2O, 18% Al_2O_3, 71% SiO_2	$K_{Na^+/H^+} = 1000$ $K_{Na^+/K^+} = 0.001$ $K_{Na^+/Li^+} = 0.001$
Li^+	15% Li_2O, 25% Al_2O_3, 60% SiO_2	$K_{Li^+/Na^+} = 0.3$ $K_{Li^+/K^+} = 0.001$
K^+	27% Na_2O, 5% Al_2O_3, 68% SiO_2	$K_{K^+/Na^+} = 0.05$

Selectivity coefficients are approximate; values found experimentally may vary substantially from the listed values. See Cammann, K. *Working With Ion-Selective Electrodes*, Springer-Verlag: Berlin, 1977.

Because an ion-selective electrode's glass membrane is very thin—it is only about 50 μm thick—they must be handled with care to avoid cracks or breakage. Glass electrodes usually are stored in a storage buffer recommended by the manufacturer, which ensures that the membrane's outer surface remains hydrated. If a glass electrode dries out, it is reconditioned by soaking for several hours in a solution that contains the analyte. The composition of a glass membrane will change over time, which affects the electrode's performance. The average lifetime for a typical glass electrode is several years.

SOLID-STATE ION-SELECTIVE ELECTRODES

A s***olid-state ion-selective electrode*** has a membrane that consists of either a polycrystalline inorganic salt or a single crystal of an inorganic salt. We can fashion a polycrystalline solid-state ion-selective electrode by sealing a 1–2 mm thick pellet of AgS—or a mixture of AgS and a second silver salt or another metal sulfide—into the end of a nonconducting plastic cylinder, filling the cylinder with an internal solution that contains the analyte, and placing a reference electrode into the internal solution. Figure 11.2.11 shows a typical design.

> The NaCl in a salt shaker is an example of polycrystalline material because it consists of many small crystals of sodium chloride. The NaCl salt plates used in IR spectroscopy (see Chapter 10), on the other hand, are an example of a single crystal of sodium chloride.

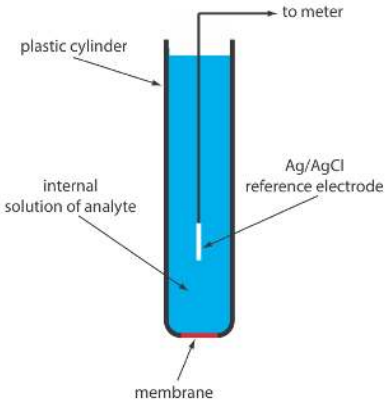


Figure 11.2.11 . Schematic diagram of a solid-state electrode. The internal solution contains a solution of analyte of fixed activity.

The membrane potential for a Ag_2S pellet develops as the result of a difference in the extent of the solubility reaction

$$Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$$

on the membrane's two sides, with charge carried across the membrane by Ag^+ ions. When we use the electrode to monitor the activity of Ag^+, the cell potential is

$$E_{cell} = K + 0.05916 \log a_{Ag^+}$$

The membrane also responds to the activity of S^{2-}, with a cell potential of

$$E_{cell} = K - \frac{0.05916}{2} \log a_{S^{2-}}$$

If we combine an insoluble silver salt, such as AgCl, with the Ag_2S, then the membrane potential also responds to the concentration of Cl^-, with a cell potential of

$$E_{cell} = K - 0.05916 \log a_{Cl^-}$$

By mixing Ag_2S with CdS, CuS, or PbS, we can make an ion-selective electrode that responds to the activity of Cd^{2+}, Cu^{2+}, or Pb^{2+}. In this case the cell potential is

$$E_{cell} = K + \frac{0.05916}{2} \ln a_{M^{2+}}$$

where $a_{M^{2+}}$ is the activity of the metal ion.

Table 11.2.2 provides examples of polycrystalline, Ag_2S-based solid-state ion-selective electrodes. The selectivity of these ion-selective electrodes depends on the relative solubility of the compounds. A Cl^- ISE using a Ag_2S/AgCl membrane is more selective for Br^- ($K_{Cl^-/Br^-} = 10^2$) and for I^- ($K_{Cl^-/I^-} = 10^6$) because AgBr and AgI are less soluble than AgCl. If the activity of Br^- is sufficiently high, AgCl at the membrane/solution interface is replaced by AgBr and the electrode's response to Cl^- decreases substantially. Most of the polycrystalline ion-selective electrodes listed in Table 11.2.2 operate over an extended range of pH levels. The equilibrium between S^{2-} and HS^- limits the analysis for S^{2-} to a pH range of 13–14.

11.2.2 . Representative Examples of Polycrystalline Solid-State Ion-Selective Electrodes

analyte	membrane composition	selectivity coefficients
Ag^+	Ag_2S	$K_{Ag^+/Cu^{2+}} = 10^{-6}$ $K_{Ag^+/Pb^{2+}} = 10^{-10}$ Hg^{2+} interferes
Cd^{2+}	CdS/Ag_2S	$K_{Cd^{2+}/Fe^{2+}} = 200$ $K_{Cd^{2+}/Pb^{2+}} = 6$ Ag^+, Hg^{2+}, and Cu^{2+} must be absent
Cu^{2+}	CuS/Ag_2S	$K_{Cu^{2+}/Fe^{3+}} = 10$ $K_{Cu^{2+}/Cu^+} = 10^{-6}$ Ag^+ and Hg^{2+} must be absent
Pb^{2+}	PbS/Ag_2S	$K_{Pb^{2+}/Fe^{3+}} = 1$ $K_{Pb^{2+}/Cd^{2+}} = 1$ Ag^+, Hg^{2+}, and Cu^{2+} must be absent
Br^-	$AgBr/Ag_2S$	$K_{Br^-/I^-} = 5000$ $K_{Br^-/Cl^-} = 0.005$ $K_{Br^-/OH^-} = 10^{-5}$ S^{2-} must be absent
Cl^-	$AgCl/Ag_2S$	$K_{Cl^-/I^-} = 10^6$ $K_{Cl^-/Br^-} = 100$ $K_{Cl^-/OH^-} = 0.01$ S^{2-} must be absent
I^-	AgI/Ag_2S	$K_{I^-/S^{2-}} = 30$ $K_{I^-/Br^-} = 10^{-4}$ $K_{I^-/Cl^-} = 10^{-6}$ $K_{I^-/OH^-} = 10^{-7}$
SCN^-	$AgSCN/Ag_2S$	$K_{SCN^-/I^-} = 10^8$ $K_{SCN^-/Br^-} = 100$ $K_{SCN^-/Cl^-} = 0.1 K_{SCN^-/OH^-} = 0.01$ S^{2-} must be absent
S^{2-}	Ag_2S	Hg^{2+} must be absent

Selectivity coefficients are approximate; values found experimentally may vary substantially from the listed values. See Cammann, K. *Working With Ion-Selective Electrodes*, Springer-Verlag: Berlin, 1977.

The membrane of a F^- ion-selective electrode is fashioned from a single crystal of LaF_3, which usually is doped with a small amount of EuF_2 to enhance the membrane's conductivity. Because EuF_2 provides only two F^- ions—compared to the three F^- ions in LaF_3—each EuF_2 produces a vacancy in the crystal's lattice. Fluoride ions pass through the membrane by moving into adjacent vacancies. As shown in Figure 11.2.11 , the LaF_3 membrane is sealed into the end of a non-conducting plastic cylinder, which contains a standard solution of F^-, typically 0.1 M NaF, and a Ag/AgCl reference electrode.

The membrane potential for a F^- ISE results from a difference in the solubility of LaF_3 on opposite sides of the membrane, with the potential given by

$$E_{cell} = K - 0.05916 \log a_{F^-}$$

One advantage of the F^- ion-selective electrode is its freedom from interference. The only significant exception is OH^- (K_{F^-/OH^-} = 0.1), which imposes a maximum pH limit for a successful analysis. Below a pH of 4 the predominate form of fluoride in solution is HF, which does not contribute to the membrane potential. For this reason, an analysis for fluoride is carried out at a pH greater than 4.

EXAMPLE 11.2.7

What is the maximum pH that we can tolerate if we need to analyze a solution in which the activity of F^- is 1×10^{-5} with an error of less than 1%?

Solution

In the presence of OH^- the cell potential is

$$E_{cell} = K - 0.05916 \left\{ a_{F^-} + K_{F^-/OH^-} \times a_{OH^-} \right\}$$

To achieve an error of less than 1%, the term $K_{F^-/OH^-} \times a_{OH^-}$ must be less than 1% of a_{F^-}; thus

$$K_{F^-/OH^-} \times a_{OH^-} \leq 0.01 \times a_{F^-}$$

$$0.10 \times a_{OH^-} \leq 0.01 \times \left(1.0 \times 10^{-5}\right)$$

Solving for a_{OH^-} gives the maximum allowable activity for OH^- as 1×10^{-6}, which corresponds to a pH of less than 8.

EXERCISE 11.2.6

Suppose you wish to use the nitrite-selective electrode in Exercise 11.2.5 to measure the activity of NO_2^-. If the activity of NO_2^- is 2.2×10^{-4}, what is the maximum pH you can tolerate if the error due to OH^- must be less than 10%? The selectivity coefficient for OH^-, $K_{NO_2^-/OH^-}$, is 630. Do you expect the electrode to have a lower pH limit? Clearly explain your answer.

Answer

In the presence of OH^- the cell potential is

$$E_{cell} = K - 0.05916 \log \left\{a_{NO_2^-} + K_{NO_2^-/OH^-} \times a_{OH^-}\right\}$$

To achieve an error of less than 10%, the term $K_{NO_2^-/OH^-} \times a_{OH^-}$ must be less than 1% of $a_{NO_2^-}$; thus

$$K_{NO_2^-/OH^-} \times a_{OH^-} \leq 0.10 \times a_{NO_2^-}$$

$$630 \times a_{OH^-} \leq 0.10 \times \left(2.2 \times 10^{-4}\right)$$

Solving for a_{OH^-} gives its maximum allowable activity as 3.5×10^{-8}, which corresponds to a pH of less than 6.54.

The electrode does have a lower pH limit. Nitrite is the conjugate weak base of HNO_2, a species to which the ISE does not respond. As shown by the ladder diagram below, at a pH of 4.15 approximately 10% of nitrite is present as HNO_2. A minimum pH of 4.5 is the usual recommendation when using a nitrite ISE. This corresponds to a NO_2^-/HNO_2 ratio of

$$\text{pH} = \text{p}K_a + \log \frac{[NO_2^-]}{[HNO_2]}$$

$$4.5 = 3.15 + \log \frac{[NO_2^-]}{[HNO_2]}$$

$$\frac{[NO_2^-]}{[HNO_2]} \approx 22$$

Thus, at a pH of 4.5 approximately 96% of nitrite is present as NO_2^-.

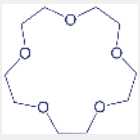
Unlike a glass membrane ion-selective electrode, a solid-state ISE does not need to be conditioned before it is used, and it may be stored dry. The surface of the electrode is subject to poisoning, as described above for a Cl^- ISE in contact with an excessive concentration of Br^-. If an electrode is poisoned, it can be returned to its original condition by sanding and polishing the crystalline membrane.

Poisoning simply means that the surface has been chemically modified, such as AgBr forming on the surface of a AgCl membrane.

LIQUID-BASED ION-SELECTIVE ELECTRODES

Another class of ion-selective electrodes uses a hydrophobic membrane that contains a liquid organic complexing agent that reacts selectively with the analyte. Three types of organic complexing agents have been used: cation exchangers, anion exchangers, and neutral ionophores. A membrane potential exists if the analyte's activity is different on the two sides of the membrane. Current is carried through the membrane by the analyte.

An ***ionophore*** is a ligand whose exterior is hydrophobic and whose interior is hydrophilic. The crown ether shown here is one example of a neutral ionophore.



One example of a ***liquid-based ion-selective electrode*** is that for Ca^{2+}, which uses a porous plastic membrane saturated with the cation exchanger di-(*n*-decyl) phosphate. As shown in Figure 11.2.12 , the membrane is placed at the end of a non-conducting cylindrical tube and is in contact with two reservoirs. The outer reservoir contains di-(*n*-decyl) phosphate in di-*n*-octylphenylphosphonate, which soaks into the porous membrane. The inner reservoir contains a standard aqueous solution of Ca^{2+} and a Ag/AgCl reference electrode. Calcium ion-selective electrodes also are available in which the di-(*n*-decyl) phosphate is immobilized in a polyvinyl chloride (PVC) membrane that eliminates the need for the outer reservoir.

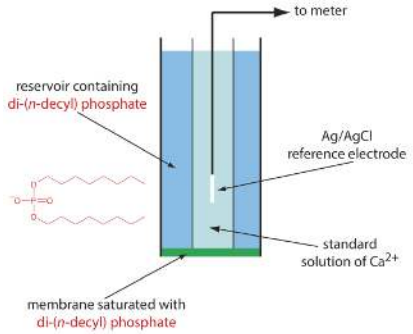


Figure 11.2.12 . Schematic diagram showing a liquid-based ion-selective electrode for Ca^{2+}. The structure of the cation exchanger, di-(*n*-decyl) phosphate, is shown in red.

The membrane potential for the Ca^{2+} ISE develops as the result of a difference in the extent of the complexation reaction

$$\mathbf{Ca^{2+}}(aq) + \mathbf{2(C_{10}H_{21}O)_2PO_2^-}(mem) \rightleftharpoons \mathbf{Ca[(C_{10}H_{21}O)_2PO_2]_2}(mem)$$

on the two sides of the membrane, where (*mem*) indicates a species that is present in the membrane. The cell potential for the Ca^{2+} ion-selective electrode is

$$E_{\text{cell}} = K + \frac{0.05916}{2}\log a_{\text{Ca}^{2+}}$$

The selectivity of this electrode for Ca^{2+} is very good, with only Zn^{2+} showing greater selectivity.

Table 11.2.3 lists the properties of several liquid-based ion-selective electrodes. An electrode using a liquid reservoir can be stored in a dilute solution of analyte and needs no additional conditioning before use. The lifetime of an electrode with a PVC membrane, however, is proportional to its exposure to aqueous solutions. For this reason these electrodes are best stored by covering the membrane with a cap along with a small amount of wetted gauze to maintain a humid environment. Before using the electrode it is conditioned in a solution of analyte for 30–60 minutes.

Table 11.2.3 . Representative Examples of Liquid-Based Ion-Selective Electrodes

analyte	membrane composition	selectivity coefficients
Ca^{2+}	di-(*n*-decyl) phosphate in PVC	$K_{Ca^{2+}/Zn^{2+}} = 1-5$ $K_{Ca^{2+}/Al^{3+}} = 0.90$ $K_{Ca^{2+}/Mn^{2+}} = 0.38$ $K_{Ca^{2+}/Cu^{2+}} = 0.070$ $K_{Ca^{2+}/Mg^{2+}} = 0.032$
K^+	valinomycin in PVC	$K_{K^+/Rb^+} = 1.9$ $K_{K^+/Cs^+} = 0.38$ $K_{K^+/Li^+} = 10^{-4}$
Li^+	ETH 149 in PVC	$K_{Li^+/H^+} = 1$ $K_{Li^+/Na^+} = 0.03$ $K_{Li^+/K^+} = 0.007$
NH_4^+	nonactin and monactin in PVC	$K_{NH_4^+/K^+} = 0.12$ $K_{NH_4^+/H^+} = 0.016$ $K_{NH_4^+/Li^+} = 0.0042$ $K_{NH_4^+/Na^+} = 0.002$
ClO_3^-	$Fe(o\text{-phen})_3^{3+}$ in *p*-nitrocymene with porous membrane	$K_{ClO_4^-/OH^-} = 1$ $K_{ClO_4^-/I^-} = 0.012$ $K_{ClO_4^-/NO_3^-} = 0.0015$ $K_{ClO_4^-/Br^-} = 5.6 \times 10^{-4}$ $K_{ClO_4^-/Cl^-} = 2.2 \times 10^{-4}$
NO_3^-	tetradodecyl ammonium nitrate in pVC	$K_{NO_3^-/Cl^-} = 0.006$ $K_{NO_3^-/F^-} = 9 \times 10^{-4}$

Selectivity coefficients are approximate; values found experimentally may vary substantially from the listed values. See Cammann, K. *Working With Ion-Selective Electrodes*, Springer-Verlag: Berlin, 1977.

GAS-SENSING ELECTRODES

A number of membrane electrodes respond to the concentration of a dissolved gas. The basic design of a ***gas-sensing electrode***, as shown in Figure 11.2.13 , consists of a thin membrane that separates the sample from an inner solution that contains an ion-selective electrode. The membrane is permeable to the gaseous analyte, but impermeable to nonvolatile components in the sample's matrix. The gaseous analyte passes through the membrane where it reacts with the inner solution, producing a species whose concentration is monitored by the ion-selective electrode. For example, in a CO_2 electrode, CO_2 diffuses across the membrane where it reacts in the inner solution to produce H_3O^+.

$$CO_2(aq) + 2H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \tag{11.2.10}$$

The change in the activity of H_3O^+ in the inner solution is monitored with a pH electrode, for which the cell potential is given by Equation 11.2.9. To find the relationship between the activity of H_3O^+ in the inner solution and the activity of CO_2 in the inner solution we rearrange the equilibrium constant expression for reaction 11.2.10; thus

$$a_{H_3O^+} = K_a \times \frac{a_{CO_2}}{a_{HCO_3^-}} \tag{11.2.11}$$

where K_a is the equilibrium constant. If the activity of HCO_3^- in the internal solution is sufficiently large, then its activity is not affected by the small amount of CO_2 that passes through the membrane. Substituting Equation 11.2.11 into Equation 11.2.9 gives

$$E_{cell} = K' + 0.05916 \log a_{co_2}$$

where K′ is a constant that includes the constant for the pH electrode, the equilibrium constant for reaction 11.2.10 and the activity of HCO_3^- in the inner solution.

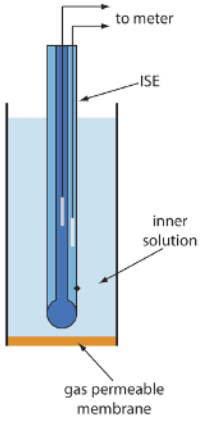


Figure 11.2.13 . Schematic diagram of a gas-sensing membrane electrode.

Table 11.2.4 lists the properties of several gas-sensing electrodes. The composition of the inner solution changes with use, and both the inner solution and the membrane must be replaced periodically. Gas-sensing electrodes are stored in a solution similar to the internal solution to minimize their exposure to atmospheric gases.

Table 11.2.4 . Representative Examples of Gas-Sensing Electrodes

analyte	inner solution	reaction in inner solution	ion-selective electrode
CO_2	10 mM $NaHCO_3$ 10 mM NaCl	$CO_2(aq) + 2H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$	glass pH ISE
HCN	10 mM $KAg(CN)_2$	$HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$	Ag_2S solid-state ISE
HF	1 M H_3O^+	$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$	F^- solid-state ISE
H_2S	pH 5 citrate buffer	$H_2S(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + H_3O^+(aq)$	Ag_2S solid state ISE
NH_3	10 mM NH_4Cl 0.1 M KNO_3	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	glass pH ISE
NO_2	20 mM $NaNO_2$ 0.1 M KNO_3	$2NO_2(aq) + 3H_2O(l) \rightleftharpoons NO_3^-(aq) + NO_2^-(aq) + 2H_3O^+(aq)$	glass pH ISE
SO_2	1 mM $NaHSO_3$ pH 5	$SO_2(aq) + 2H_2O(l) \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq)$	glass pH ISE

Source: Cammann, K. *Working With Ion-Selective Electrodes*, Springer-Verlag: Berlin, 1977.

POTENTIOMETRIC BIOSENSORS

The approach for developing gas-sensing electrodes can be modified to create potentiometric electrodes that respond to a biochemically important species. The most common class of potentiometric biosensors are ***enzyme electrodes***, in which we trap or immobilize an enzyme at the surface of a potentiometric electrode. The analyte's reaction with the enzyme produces a product whose concentration is monitored by the potentiometric electrode. Potentiometric biosensors also have been designed around other biologically active species, including antibodies, bacterial particles, tissues, and hormone receptors.

One example of an enzyme electrode is the urea electrode, which is based on the catalytic hydrolysis of urea by urease

$$CO(NH_2)_2(aq) + 2H_2O(l) \rightleftharpoons 2NH_4^+(aq) + CO_3^-(aq)$$

Figure 11.2.14 shows one version of the urea electrode, which modifies a gas-sensing NH_3 electrode by adding a dialysis membrane that traps a pH 7.0 buffered solution of urease between the dialysis membrane and the gas permeable membrane [(a) Papastathopoulos, D. S.; Rechnitz, G. A. *Anal. Chim. Acta* **1975**, *79*, 17–26; (b) Riechel, T. L. *J. Chem. Educ*. **1984**, *61*, 640–642]. An NH_3 electrode, as shown in Table 11.2.4 , uses a gas-permeable membrane and a glass pH electrode. The NH_3 diffuses across the membrane where it changes the pH of the internal solution.

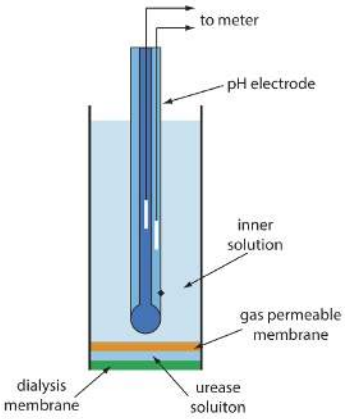


Figure 11.2.14 . Schematic diagram showing an enzyme-based potentiometric biosensor for urea. A solution of the enzyme urease is trapped between a dialysis membrane and a gas permeable membrane. Urea diffuses across the dialysis membrane and reacts with urease, producing NH_3 that diffuses across the gas permeable membrane. The resulting change in the internal solution's pH is measured with the pH electrode.

When immersed in the sample, urea diffuses through the dialysis membrane where it reacts with the enzyme urease to form the ammonium ion, $\mathbf{NH_4^+}$, which is in equilibrium with NH_3.

$$\mathbf{NH_4^+}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{NH_3}(aq)$$

The NH_3, in turn, diffuses through the gas permeable membrane where a pH electrode measures the resulting change in pH. The electrode's response to the concentration of urea is

$$E_{\text{cell}} = K - 0.05916 \log a_{\text{urea}} \tag{11.2.12}$$

Another version of the urea electrode (Figure 11.2.15) immobilizes the enzyme urease in a polymer membrane formed directly on the tip of a glass pH electrode [Tor, R.; Freeman, A. *Anal. Chem.* **1986**, *58*, 1042–1046]. In this case the response of the electrode is

$$\mathbf{pH} = Ka_{\text{urea}} \tag{11.2.13}$$

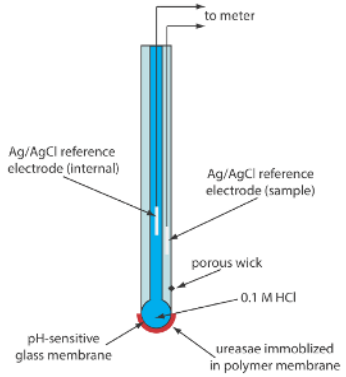


Figure 11.2.15 . Schematic diagram of an enzyme-based potentiometric biosensor for urea in which urease is immobilized in a polymer membrane coated onto the pH-sensitive glass membrane of a pH electrode.

Few potentiometric biosensors are available commercially. As shown in Figure 11.2.14 and Figure 11.2.15 , however, it is possible to convert an ion-selective electrode or a gas-sensing electrode into a biosensor. Several representative examples are described in Table 11.2.5 , and additional examples can be found in this chapter's additional resources.

Table 11.2.5 . Representative Examples of Potentiometric Biosensors

analyte	biologically active phase	substance determined
5′-AMP	AMP-deaminase (E)	NH_3
L-arginine	arginine and urease (E)	NH_3
asparagine	asparaginase (E)	NH_4^+
L-cysteine	*Proteus morganii* (B)	H_2S
L-glutamate	yellow squash (T)	CO_2
L-glutamine	*Sarcina flava* (B)	NH_3
oxalate	oxalate decarboxylase (E)	CO_2
penicillin	penicllinase (E)	H_3O^+
L-phenylalanine	L-amino acid oxidase/horseradish peroxidase (E)	I^-
sugars	bacteria from dental plaque (B)	H_3O^+
urea	urease (E)	NH_3 or H_3O^+

Source: Complied from Cammann, K. *Working With Ion-Selective Electrodes*, Springer-Verlag: Berlin, 1977 and Lunte, C. E.; Heineman, W. R. "Electrochemical techniques in Bioanalysis," in Steckham, E. ed. *Topics in Current Chemistry*, Vol. 143, Springer-Verlag: Berlin, 1988, p.8.
Abbreviations for biologically active phase: E = enzyme; B = bacterial particle; T = tissue.

QUANTITATIVE APPLICATIONS

The potentiometric determination of an analyte's concentration is one of the most common quantitative analytical techniques. Perhaps the most frequent analytical measurement is the determination of a solution's pH, a measurement we will consider in more detail later in this section. Other areas where potentiometry is important are clinical chemistry, environmental chemistry, and potentiometric titrations. Before we consider representative applications, however, we need to examine more closely the relationship between cell potential and the analyte's concentration and methods for standardizing potentiometric measurements.

ACTIVITY AND CONCENTRATION

The Nernst equation relates the cell potential to the analyte's activity. For example, the Nernst equation for a metallic electrode of the first kind is

$$E_{cell} = K + \frac{0.05916}{n} \log a_{M^{n+}} \tag{11.2.14}$$

where $a_{M^{n+}}$ is the metal ion's activity. When we use a potentiometric electrode, however, our goal is to determine the analyte's concentration. As we learned in Chapter 6, an ion's activity is the product of its concentration, $[M^{n+}]$, and a matrix-dependent activity coefficient, $\gamma_{M^{n+}}$.

$$a_{M^{n+}} = [M^{n+}]\,\gamma_{M^{n+}} \tag{11.2.15}$$

Substituting Equation 11.2.15 into Equation 11.2.14 and rearranging, gives

$$E_{cell} = K + \frac{0.05916}{n} \log \gamma_{M^{n+}} + \frac{0.05916}{n} \log [M^{n+}] \tag{11.2.16}$$

We can solve Equation 11.2.16 for the metal ion's concentration if we know the value for its activity coefficient. Unfortunately, if we do not know the exact ionic composition of the sample's matrix—which is the usual situation—then we cannot calculate the value of $\gamma_{M^{n+}}$. There is a solution to this dilemma. If we design our system so that the standards and the samples have an identical matrix, then the value of $\gamma_{M^{n+}}$ remains constant and Equation 11.2.16 simplifies to

$$E_{cell} = K' + \frac{0.05916}{n} \log [M^{n+}]$$

where K' includes the activity coefficient.

QUANTITATIVE ANALYSIS USING EXTERNAL STANDARDS

Before we can determine the concentration of analyte in a sample, we must standardize the electrode. If the electrode's response obeys the Nernst equation, then we can determine the constant K using a single external standard. Because a small deviation from the ideal slope of $\pm RT/nF$ or $\pm RT/zF$ is not unexpected, we usually use two or more external standards.

> To review the use of external standards, see Chapter 5.3.

In the absence of interferents, a calibration curve of E_{cell} versus $\log a_A$, where A is the analyte, is a straight-line. A plot of E_{cell} versus $\log[A]$, however, may show curvature at higher concentrations of analyte as a result of a matrix-dependent change in the analyte's activity coefficient. To maintain a consistent matrix we add a high concentration of an inert electrolyte to all samples and standards. If the concentration of added electrolyte is sufficient, then the difference between the sample's matrix and the matrix of the standards will not affect the ionic strength and the activity coefficient essentially remains constant. The inert electrolyte added to the sample and the standards is called a ***total ionic strength adjustment buffer*** (TISAB).

EXAMPLE 11.2.8

The concentration of Ca^{2+} in a water sample is determined using the method of external standards. The ionic strength of the samples and the standards is maintained at a nearly constant level by making each solution 0.5 M in KNO_3. The measured cell potentials for the external standards are shown in the following table.

$[Ca^{2+}]$ (M)	E_{cell} (V)
1.00×10^{-5}	–0.125
5.00×10^{-5}	–0.103
1.00×10^{-4}	–0.093
5.00×10^{-4}	–0.072
1.00×10^{-3}	–0.063
5.00×10^{-3}	–0.043
1.00×10^{-2}	–0.033

What is the concentration of Ca^{2+} in a water sample if its cell potential is found to be –0.084 V?

Solution

Linear regression gives the calibration curve in Figure 11.2.16 , with an equation of

$$E_{cell} = 0.027 + 0.0303 \log [Ca^{2+}]$$

Substituting the sample's cell potential gives the concentration of Ca^{2+} as 2.17×10^{-4} M. Note that the slope of the calibration curve, which is 0.0303, is slightly larger than its ideal value of 0.05916/2 = 0.02958; this is not unusual and is one reason for using multiple standards.

One reason that it is not unusual to find that the experimental slope deviates from its ideal value of 0.05916/n is that this ideal value assumes that the temperature is 25°C.

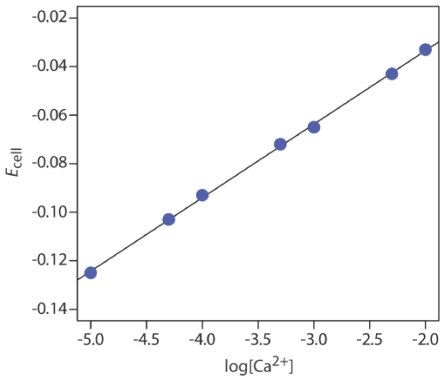


Figure 11.2.16 . Calibration curve for the data in Example 11.2.8 .

QUANTITATIVE ANALYSIS USING THE METHOD OF STANDARD ADDITIONS

Another approach to calibrating a potentiometric electrode is the method of standard additions. First, we transfer a sample with a volume of V_{samp} and an analyte concentration of C_{samp} into a beaker and measure the potential, $(E_{cell})_{samp}$. Next, we make a standard addition by adding to the sample a small volume, V_{std}, of a standard that contains a known concentration of analyte, C_{std}, and measure the potential, (E_{cell})std. If V_{std} is significantly smaller than V_{samp}, then we can safely ignore the change in the sample's matrix and assume that the

analyte's activity coefficient is constant. Example 11.2.9 demonstrates how we can use a one-point standard addition to determine the concentration of analyte in a sample.

To review the method of standard additions, see Chapter 5.3.

EXAMPLE 11.2.9

The concentration of Ca^{2+} in a sample of sea water is determined using a Ca ion-selective electrode and a one-point standard addition. A 10.00-mL sample is transferred to a 100-mL volumetric flask and diluted to volume. A 50.00-mL aliquot of the sample is placed in a beaker with the Ca ISE and a reference electrode, and the potential is measured as –0.05290 V. After adding a 1.00-mL aliquot of a 5.00×10^{-2} M standard solution of Ca^{2+} the potential is –0.04417 V. What is the concentration of Ca^{2+} in the sample of sea water?

Solution

To begin, we write the Nernst equation before and after adding the standard addition. The cell potential for the sample is

$$(E_{cell})_{samp} = K + \frac{0.05916}{2} \log C_{samp}$$

and that following the standard addition is

$$(E_{cell})_{std} = K + \frac{0.05916}{2} \log \left\{ \frac{V_{samp}}{V_{tot}} C_{samp} + \frac{V_{std}}{V_{tot}} C_{std} \right\}$$

where V_{tot} is the total volume (V_{samp} + V_{std}) after the standard addition. Subtracting the first equation from the second equation gives

$$\Delta E = (E_{cell})_{std} - (E_{cell})_{samp} = \frac{0.05916}{2} \log \left\{ \frac{V_{samp}}{V_{tot}} C_{samp} + \frac{V_{std}}{V_{tot}} C_{std} \right\} - \frac{0.05916}{2} \log C_{samp}$$

Rearranging this equation leaves us with

$$\frac{2\Delta E_{cell}}{0.05916} = \log \left\{ \frac{V_{samp}}{V_{tot}} + \frac{V_{std} C_{std}}{V_{tot} C_{samp}} \right\}$$

Substituting known values for ΔE, V_{samp}, V_{std}, V_{tot} and C_{std},

$$\frac{2 \times \{-0.04417 - (-0.05290)\}}{0.05916} = \log \left\{ \frac{50.00 \text{ mL}}{51.00 \text{ mL}} + \frac{(1.00 \text{ mL})(5.00 \times 10^{-2} \text{M})}{(51.00 \text{ mL}) C_{samp}} \right\}$$

$$0.2951 = \log \left\{ 0.9804 + \frac{9.804 \times 10^{-4}}{C_{samp}} \right\}$$

and taking the inverse log of both sides gives

$$1.973 = 0.9804 + \frac{9.804 \times 10^{-4}}{C_{samp}}$$

Finally, solving for C_{samp} gives the concentration of Ca^{2+} as 9.88×10^{-4} M. Because we diluted the original sample of seawater by a factor of 10, the concentration of Ca^{2+} in the seawater sample is 9.88×10^{-3} M.

FREE IONS VERSUS COMPLEXED IONS

Most potentiometric electrodes are selective toward the free, uncomplexed form of the analyte, and do not respond to any of the analyte's complexed forms. This selectivity provides potentiometric electrodes with a significant advantage over other quantitative methods of analysis if we need to determine the concentration of free ions. For example, calcium is present in urine both as free Ca^{2+} ions and as protein-bound Ca^{2+} ions. If we analyze a urine sample using atomic absorption spectroscopy, the signal is propor- tional to the total concentration of Ca^{2+} because both free and bound calcium are atomized. Analyzing urine with a Ca^{2+} ISE, however, gives a signal that is a function of only free Ca^{2+} ions because the protein-bound Ca^{2+} can not interact with the electrode's membrane.

The best way to appreciate the theoretical and the practical details discussed in this section is to carefully examine a typical analytical method. Although each method is unique, the following description of the determination of F^- in toothpaste provides an instructive example of a typical procedure. The description here is based on Kennedy, J. H. *Analytical Chemistry— Practice*, Harcourt Brace Jaovanovich: San Diego, 1984, p. 117–118.

REPRESENTATIVE METHOD 11.2.1: DETERMINATION OF FLUORIDE IN TOOTHPASTE

Description of the Method

The concentration of fluoride in toothpastes that contains soluble F^- is determined with a F^- ion-selective electrode using a calibration curve prepared with external standards. Although the F^- ISE is very selective (only OH^- with a K_{F^-/OH^-} of 0.1 is a significant interferent), Fe^{3+} and Al^{3+} interfere with the analysis because they form soluble fluoride complexes that do not interact with the ion-selective electrode's membrane. This interference is minimized by reacting any Fe^{3+} and Al^{3+} with a suitable complexing agent.

Procedure

Prepare 1 L of a standard solution of 1.00% w/v SnF_2 and transfer it to a plastic bottle for storage. Using this solution, prepare 100 mL each of standards that contain 0.32%, 0.36%, 0.40%, 0.44% and 0.48% w/v SnF_2, adding 400 mg of malic acid to each solution as a stabilizer. Transfer the standards to plastic bottles for storage. Prepare a total ionic strength adjustment buffer (TISAB) by mixing 500 mL of water, 57 mL of glacial acetic acid, 58 g of NaCl, and 4 g of disodium DCTA (*trans*-1,2-cyclohexanetetraacetic acid) in a 1-L beaker, stirring until dissolved. Cool the beaker in a water bath and add 5 M NaOH until the pH is between 5–5.5. Transfer the contents of the beaker to a 1-L volumetric flask and dilute to volume. Prepare each external standard by placing approximately 1 g of a fluoride-free toothpaste, 30 mL of distilled water, and 1.00 mL of standard into a 50-mL plastic beaker and mix vigorously for two min with a stir bar. Quantitatively transfer the resulting suspension to a 100-mL volumetric flask along with 50 mL of TISAB and dilute to volume with distilled water. Store the entire external standard in a 250-mL plastic beaker until you are ready to measure the potential. Prepare toothpaste samples by obtaining an approximately 1-g portion and treating in the same manner as the standards. Measure the cell potential for the external standards and the samples using a F^- ion-selective electrode and an appropriate reference electrode. When measuring the potential, stir the solution and allow two to three minutes to reach a stable potential. Report the concentration of F^- in the toothpaste %w/w SnF_2.

Questions

1. The total ionic strength adjustment buffer serves several purposes in this procedure. Identify these purposes.

The composition of the TISAB has three purposes:

(a) The high concentration of NaCl (the final solutions are approximately 1 M NaCl) ensures that the ionic strength of each external standard and each sample is essentially identical. Because the activity coefficient for fluoride is the same in all solutions, we can write the Nernst equation in terms of fluoride's concentration instead of its activity.

(b) The combination of glacial acetic acid and NaOH creates an acetic acid/acetate buffer of pH 5–5.5. As shown in Figure 11.2.17 , the pH of this buffer is high enough to ensure that the predominate form of fluoride is F^- instead of HF. This pH also is sufficiently acidic that it avoids an interference from OH^- (see Example 11.2.8)).

(c) DCTA is added as a complexing agent for Fe^{3+} or Al^{3+}, preventing the formation of $\mathbf{FeF_6^{3-}}$ or $\mathbf{AlF_6^{3-}}$.

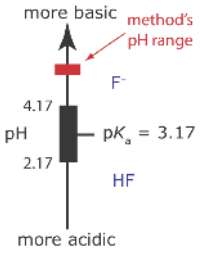


Figure 11.2.17 . Ladder diagram for HF/F^-. Maintaining a pH greater than 4.2 ensures that the only significant form of fluoride is F^-.

2. Why is a fluoride-free toothpaste added to the standard solutions?

Adding a fluoride-free toothpaste protects against any unaccounted for matrix effects that might influence the ion-selective electrode's response. This assumes, of course, that the matrices of the two toothpastes are otherwise similar.

3. The procedure specifies that the standards and the sample should be stored in plastic containers. Why is it a bad idea to store the solutions in glass containers?

The fluoride ion is capable of reacting with glass to form SiF_4.

4. Suppose your calibration curve has a slope of –57.98 mV for each 10-fold change in the concentration of F^-. The ideal slope from the Nernst equation is –59.16 mV per 10-fold change in concentration. What effect does this have on the quantitative analysis for fluoride in toothpaste?

No effect at all! This is why we prepare a calibration curve using multiple standards.

MEASUREMENT OF PH

With the availability of inexpensive glass pH electrodes and pH meters, the determination of pH is one of the most common quantitative analytical measurements. The potentiometric determination of pH, however, is not without complications, several of which we discuss in this section.

One complication is confusion over the meaning of pH [Kristensen, H. B.; Saloman, A.; Kokholm, G. *Anal. Chem.* **1991**, *63*, 885A–891A]. The conventional definition of pH in most general chemistry textbooks is

$$\mathrm{pH} = -\log\left[\mathrm{H}^+\right] \tag{11.2.17}$$

As we now know, pH actually is a measure of the activity of H^+.

$$\mathrm{pH} = -\log a_{\mathrm{H}^+} \tag{11.2.18}$$

> Try this experiment—find several general chemistry textbooks and look up *pH* in each textbook's index. Turn to the appropriate pages and see how it is defined. Next, look up *activity* or *activity coefficient* in each textbook's index and see if these terms are indexed.

Equation 11.2.17 only approximates the true pH. If we calculate the pH of 0.1 M HCl using Equation 11.2.17, we obtain a value of 1.00; the solution's actual pH, as defined by Equation 11.2.18, is 1.1 [Hawkes, S. J. *J. Chem. Educ.* **1994**, *71*, 747–749]. The activity and the concentration of H^+ are not the same in 0.1 M HCl because the activity coefficient for H^+ is not 1.00 in this matrix. Figure 11.2.18 shows a more colorful demonstration of the difference between activity and concentration.

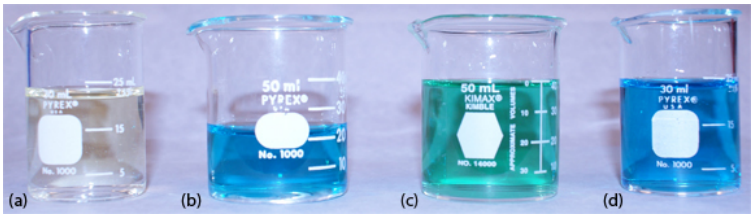


Figure 11.2.18 . A demonstration of the difference between activity and concentration using the indicator methyl green. The indicator is pale yellow in its acid form (beaker a: 1.0 M HCl) and is blue in its base form (beaker d: H_2O). In 10 mM HCl the indicator is in its base form (beaker b: 20 mL of 10 mM HCl with 3 drops of methyl green). Adding 20 mL of 5 M LiCl to this solution shifts the indicator's color to green (beaker c); although the concentration of HCl is cut in half to 5 mM, the activity of H^+ has increased as evidenced by the green color that is intermediate between the indicator's pale yellow, acid form and its blue, base form. The demonstration shown here is adapted from McCarty, C. G.; Vitz, E. "pH Paradoxes: Demonstrating That It Is Not True That pH ≡ –log[H^+]," *J. Chem. Educ.* **2006**, *83*, 752–757. This paper provides several additional demonstrations that illustrate the difference between concentration and activity.

A second complication in measuring pH is the uncertainty in the relationship between potential and activity. For a glass membrane electrode, the cell potential, $(E_{\mathrm{cell}})_{\mathrm{samp}}$, for a sample of unknown pH is

$$(E_{\mathrm{cell}})_{\mathrm{samp}} = K - \frac{RT}{F}\ln\frac{1}{a_{\mathrm{H}^+}} = K - \frac{2.303RT}{F}\mathrm{pH}_{\mathrm{samp}} \tag{11.2.19}$$

where K includes the potential of the reference electrode, the asymmetry potential of the glass membrane, and any junction potentials in the electrochemical cell. All the contributions to K are subject to uncertainty, and may change from day-to-day, as well as from electrode-to-electrode. For this reason, before using a pH electrode we calibrate it using a standard buffer of known pH. The cell potential for the standard, $(E_{\mathrm{cell}})_{\mathrm{std}}$, is

$$(E_{\mathrm{cell}})_{\mathrm{std}} = K - \frac{2.303RT}{F}\mathrm{pH}_{\mathrm{std}} \tag{11.2.20}$$

where $\mathrm{pH}_{\mathrm{std}}$ is the standard's pH. Subtracting Equation 11.2.20 from Equation 11.2.19 and solving for $\mathrm{pH}_{\mathrm{samp}}$ gives

$$\mathrm{pH}_{\mathrm{samp}} = \mathrm{pH}_{\mathrm{std}} - \frac{\left\{(E_{\mathrm{cell}})_{\mathrm{samp}} - (E_{\mathrm{cell}})_{\mathrm{std}}\right\}F}{2.303RT} \tag{11.2.21}$$

which is the operational definition of pH adopted by the International Union of Pure and Applied Chemistry [Covington, A. K.; Bates, R. B.; Durst, R. A. *Pure & Appl. Chem.* **1985**, *57*, 531–542].

Calibrating a pH electrode presents a third complication because we need a standard with an accurately known activity for H^+. Table 11.2.6 provides pH values for several primary standard buffer solutions accepted by the National Institute of Standards and Technology.

Table 11.2.6 . pH Values for Selected NIST Primary Standard Buffers

temp (°C)	saturated (at 25°C) KHC_4H4O_7 (tartrate)	0.05 m $KH_2C_6H_5O_7$ (citrate)	0.05 m $KHC_8H_4O_4$ (phthlate)	0.025 m KH_2PO_4, 0.025 m $NaHPO_4$	0.008695 m KH_2PO_4, 0.03043 m Na_2HPO_4	0.01 m $Na_4B_4O_7$	0.025 m $NaHCO_3$, 0.025 m Na_2CO_3
0	—	3.863	4.003	6.984	7.534	9.464	10.317
5	—	3.840	3.999	6.951	7.500	9.395	10.245
10	—	3.820	3.998	6.923	7.472	9.332	10.179
15	—	3.802	3.999	6.900	7.448	9.276	10.118
20	—	3.788	4.002	6.881	7.429	9.225	10.062
25	3.557	3.776	4.008	6.865	7.413	9.180	10.012
30	3.552	3.766	4.015	6.854	7.400	9.139	9.966
35	3.549	3.759	4.024	6.844	7.389	9.012	9.925
40	3.547	3.753	4.035	6.838	7.380	9.068	9.889
45	3.547	3.750	4.047	6.834	7.373	9.038	9.856
50	3.549	3.749	4.060	6.833	7.367	9.011	9.828

Source: Values taken from Bates, R. G. *Determination of pH: Theory and Practice*, 2nd ed. Wiley: New York, 1973. See also Buck, R. P., et. al."Measurement of pH. Definition, Standards, and Procedures," *Pure. Appl. Chem.* **2002**, *74*, 2169–2200. All concentrations are molal (m).

To standardize a pH electrode using two buffers, choose one near a pH of 7 and one that is more acidic or basic depending on your sample's expected pH. Rinse your pH electrode in deionized water, blot it dry with a laboratory wipe, and place it in the buffer with the pH closest to 7. Swirl the pH electrode and allow it to equilibrate until you obtain a stable reading. Adjust the "Standardize" or "Calibrate" knob until the meter displays the correct pH. Rinse and dry the electrode, and place it in the second buffer. After the electrode equilibrates, adjust the "Slope" or "Temperature" knob until the meter displays the correct pH.

Some pH meters can compensate for a change in temperature. To use this feature, place a temperature probe in the sample and connect it to the pH meter. Adjust the "Temperature" knob to the solution's temperature and calibrate the pH meter using the "Calibrate" and "Slope" controls. As you are using the pH electrode, the pH meter compensates for any change in the sample's temperature by adjusting the slope of the calibration curve using a Nernstian response of $2.303RT/F$.

CLINICAL APPLICATIONS

Because of their selectivity for analytes in complex matricies, ion-selective electrodes are important sensors for clinical samples. The most common analytes are electrolytes, such as Na^+, K^+, Ca^{2+}, H^+, and Cl^-, and dissolved gases such as CO_2. For extracellular fluids, such as blood and urine, the analysis can be made *in vitro*. An *in situ* analysis, however, requires a much smaller electrode that we can insert directly into a cell. Liquid-based membrane microelectrodes with tip diameters smaller than 1 μm are constructed by heating and drawing out a hard-glass capillary tube with an initial diameter of approximately 1–2 mm (Figure 11.2.19). The microelectrode's tip is made hydrophobic by dipping into a solution of dichlorodimethyl silane, and an inner solution appropriate for the analyte and a Ag/AgCl wire reference electrode are placed within the microelectrode. The microelectrode is dipped into a solution of the liquid complexing agent, which through capillary action draws a small volume of the liquid complexing agent into the tip. Potentiometric microelectrodes have been developed for a number of clinically important analytes, including H^+, K^+, Na^+, Ca^{2+}, Cl^-, and I^- [Bakker, E.; Pretsch, E. *Trends Anal. Chem.* **2008**, *27*, 612–618].

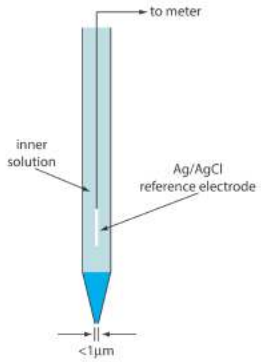


Figure 11.2.19 . Schematic diagram of a liquid-based ion-selective microelectrode.

ENVIRONMENTAL APPLICATIONS

Although ion-selective electrodes are used in environmental analysis, their application is not as widespread as in clinical analysis. Although standard potentiometric methods are available for the analysis of CN^-, F^-, NH_3, and NO_3^- in water and wastewater, other analytical methods generally provide better detection limits. One potential advantage of an ion-selective electrode is the ability to incorporate it into a flow cell for the continuous monitoring of wastewater streams.

POTENTIOMETRIC TITRATIONS

One method for determining the equivalence point of an acid–base titration is to use a pH electrode to monitor the change in pH during the titration. A potentiometric determination of the equivalence point is possible for acid–base, complexation, redox, and precipitation titrations, as well as for titrations in aqueous and nonaqueous solvents. Acid–base, complexation, and precipitation potentiometric titrations usually are monitored with an ion-selective electrode that responds the analyte, although an electrode that responds to the titrant or a reaction product also can be used. A redox electrode, such as a Pt wire, and a reference electrode are used for potentiometric redox titrations. More details about potentiometric titrations are found in Chapter 9.

EVALUATION

SCALE OF OPERATION

The working range for most ion-selective electrodes is from a maximum concentration of 0.1–1 M to a minimum concentration of $10^{-5} - 10^{-11}$ M [(a) Bakker, E.; Pretsch, E. *Anal. Chem.* **2002**, *74*, 420A–426A; (b) Bakker, E.; Pretsch, E. *Trends Anal. Chem.* **2005**, *24*, 199–207]. This broad working range extends from major analytes to ultratrace analytes, and is significantly greater than many other analytical techniques. To use a conventional ion-selective electrode we need a minimum sample volume of several mL (a macro sample). Microelectrodes, such as the one shown in Figure 11.2.19 , are used with an ultramicro sample, although care is needed to ensure that the sample is representative of the original sample.

ACCURACY

The accuracy of a potentiometric analysis is limited by the error in measuring E_{cell}. Several factors contribute to this measurement error, including the contribution to the potential from interfering ions, the finite current that passes through the cell while we measure the potential, differences between the analyte's activity coefficient in the samples and the standard solutions, and junction potentials. We can limit the effect of an interfering ion by including a separation step before the potentiometric analysis. Modern high impedance potentiometers minimize the amount of current that passes through the electrochemical cell. Finally, we can minimize the errors due to activity coefficients and junction potentials by matching the matrix of the standards to that of the sample. Even in the best circumstances, however, a difference of approximately ±1 mV for samples with equal concentrations of analyte is not unusual.

We can evaluate the effect of uncertainty on the accuracy of a potentiometric measurement by using a propagation of uncertainty. For a membrane ion-selective electrode the general expression for potential is

$$E_{cell} = K + \frac{RT}{zF}\ln[A]$$

where z is the analyte's, A, charge. From Table 4.3.1 in Chapter 4, the uncertainty in the cell potential, ΔE_{cell} is

$$\triangle E_{cell} = \frac{RT}{zF} \times \frac{\Delta[A]}{[A]}$$

Rearranging and multiplying through by 100 gives the percent relative error in concentration as

$$\%\ \text{relative error} = \frac{\Delta[A]}{[A]} \times 100 = \frac{\triangle E_{cell}}{RT/zF} \times 100 \qquad (11.2.22)$$

The relative error in concentration, therefore, is a function of the measurement error for the electrode's potential, ΔE_{cell}, and the analyte's charge. Table 11.2.7 provides representative values for ions with charges of ±1 and ±2 at a temperature of 25°C. Accuracies of 1–5% for monovalent ions and 2–10% for divalent ions are typical. Although Equation 11.2.22 applies to membrane electrodes, we can use if for a metallic electrode by replacing z with n.

Table 11.2.7 . Relationship Between the Uncertainty in Measuring E_{cell} and the Relative Error in the Analyte's Concentration

$\Delta E_{cell}(\pm \text{ mV})$	% relative error when $z = \pm 1$	% relative error when $z = \pm 2$
0.1	±0.4	±0.8
0.5	±1.9	±3.9
1.0	±3.0	±7.8
1.5	±5.8	±11.1
2.0	±7.8	±15.6

PRECISION

Precision in potentiometry is limited by variations in temperature and the sensitivity of the potentiometer. Under most conditions—and when using a simple, general-purpose potentiometer—we can measure the potential with a repeatability of ±0.1 mV. Using Table 11.2.7 , this corresponds to an uncertainty of ±0.4% for monovalent analytes and ±0.8% for divalent analytes. The reproducibility of potentiometric measurements is about a factor of ten poorer.

SENSITIVITY

The sensitivity of a potentiometric analysis is determined by the term *RT*/*nF* or *RT*/*zF* in the Nernst equation. Sensitivity is best for smaller values of *n* or *z*.

SELECTIVITY

As described earlier, most ion-selective electrodes respond to more than one analyte; the selectivity for the analyte, however, often is significantly greater than the sensitivity for the interfering ions. The manufacturer of an ion-selective usually provides an ISE's selectivity coefficients, which allows us to determine whether a potentiometric analysis is feasible for a given sample.

TIME, COST, AND EQUIPMENT

In comparison to other techniques, potentiometry provides a rapid, relatively low-cost means for analyzing samples. The limiting factor when analyzing a large number of samples is the need to rinse the electrode between samples. The use of inexpensive, disposable ion-selective electrodes can increase a lab's sample throughput. Figure 11.2.20 shows one example of a disposable ISE for Ag^+ [Tymecki, L.; Zwierkowska, E.; Głąb, S.; Koncki, R. *Sens. Actuators B* **2003**, *96*, 482–488]. Commercial instruments for measuring pH or potential are available in a variety of price ranges, and includes portable models for use in the field.

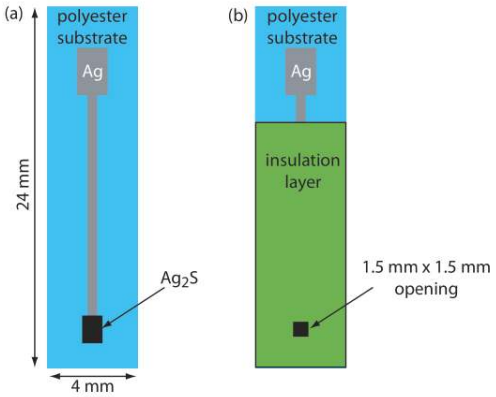


Figure 11.2.20 . Schematic diagram of a disposable ion-selective electrode created by screen-printing. In (a) a thin film of conducting silver is printed on a polyester substrate and a film of Ag_2S overlaid near the bottom. In (b) an insulation layer with a small opening is layered on top exposes a portion of the Ag_2S membrane that is immersed in the sample. The top of the polyester substrate remains uncoated, which allows us to connect the electrode to a potentiometer through the Ag film. The small inset shows the electrode's actual size.

11.3: COULOMETRIC METHODS

In a potentiometric method of analysis we determine an analyte's concentration by measuring the potential of an electrochemical cell under static conditions in which no current flows and the concentrations of species in the electrochemical cell remain fixed. Dynamic techniques, in which current passes through the electrochemical cell and concentrations change, also are important electrochemical methods of analysis. In this section we consider coulometry. Voltammetry and amperometry are covered in Chapter 11.4.

Coulometry is based on an exhaustive electrolysis of the analyte. By exhaustive we mean that the analyte is oxidized or reduced completely at the working electrode, or that it reacts completely with a reagent generated at the working electrode. There are two forms of coulometry: ***controlled-potential coulometry***, in which we apply a constant potential to the electrochemical cell, and ***controlled-current coulometry***, in which we pass a constant current through the electrochemical cell.

During an electrolysis, the total charge, Q, in coulombs, that passes through the electrochemical cell is proportional to the absolute amount of analyte by ***Faraday's law***

$$Q = nFN_A \tag{11.3.1}$$

where n is the number of electrons per mole of analyte, F is Faraday's constant (96 487 C mol^{-1}), and N_A is the moles of analyte. A coulomb is equivalent to an A•sec; thus, for a constant current, i, the total charge is

$$Q = it_e \tag{11.3.2}$$

where t_e is the electrolysis time. If the current varies with time, as it does in controlled-potential coulometry, then the total charge is

$$Q = \int_0^{t_e} i(t)dt \tag{11.3.3}$$

In coulometry, we monitor current as a function of time and use either Equation 11.3.2 or Equation 11.3.3 to calculate Q. Knowing the total charge, we then use Equation 11.3.1 to determine the moles of analyte. To obtain an accurate value for N_A, all the current must oxidize or reduce the analyte; that is, coulometry requires 100% ***current efficiency*** or an accurate measurement of the current efficiency using a standard.

> Current efficiency is the percentage of current that actually leads to the analyte's oxidation or reduction.

CONTROLLED-POTENTIAL COULOMETRY

The easiest way to ensure 100% current efficiency is to hold the working electrode at a constant potential where the analyte is oxidized or reduced completely and where no potential interfering species are oxidized or reduced. As electrolysis progresses, the analyte's concentration and the current decrease. The resulting current-versus-time profile for controlled-potential coulometry is shown in Figure 11.3.1 . Integrating the area under the curve (Equation 11.3.3) from t = 0 to $t = t_e$ gives the total charge. In this section we consider the experimental parameters and instrumentation needed to develop a controlled-potential coulometric method of analysis.

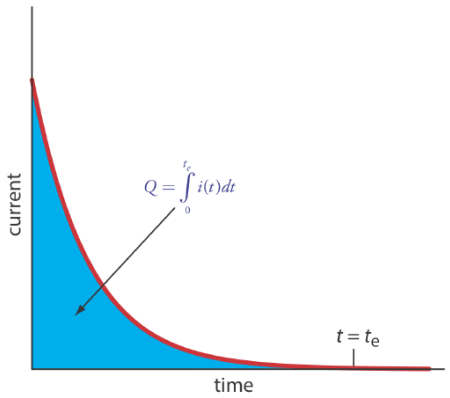


Figure 11.3.1 . Current versus time for a controlled-potential coulometric analysis. The measured current is shown by the red curve. The integrated area under the curve, shown in blue, is the total charge.

SELECTING A CONSTANT POTENTIAL

To understand how an appropriate potential for the working electrode is selected, let's develop a constant-potential coulometric method for Cu^{2+} based on its reduction to copper metal at a Pt working electrode.

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \tag{11.3.4}$$

Figure 11.3.2 shows a ladder diagram for an aqueous solution of Cu^{2+}. From the ladder diagram we know that reaction 11.3.4 is favored when the working electrode's potential is more negative than +0.342 V versus the standard hydrogen electrode. To ensure a 100% current efficiency, however, the potential must be sufficiently more positive than +0.000 V so that the reduction of H_3O^+ to H_2 does not contribute significantly to the total current flowing through the electrochemical cell.

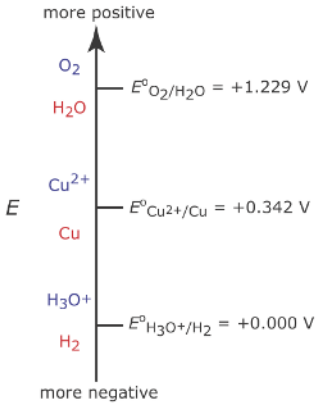


Figure 11.3.2 . Ladder diagram for an aqueous solution of Cu^{2+} showing steps for the reductions of O_2 to H_2O, of Cu^{2+} to Cu, and of H_3O^+ to H_2. For each step, the oxidized species is in blue and the reduced species is in red

We can use the Nernst equation for reaction 11.3.4 to estimate the minimum potential for quantitatively reducing Cu^{2+}.

$$E = E^\circ_{Cu^{2+}/Cu} - \frac{0.05916}{2} \log \frac{1}{[Cu^{2+}]} \tag{11.3.5}$$

So why are we using the concentration of Cu^{2+} in Equation 11.3.5 instead of its activity? In potentiometry we use activity because we use E_{cell} to determine the analyte's concentration. Here we use the Nernst equation to help us select an appropriate potential. Once we identify a potential, we can adjust its value as needed to ensure a quantitative reduction of Cu^{2+}. In addition, in coulometry the analyte's concentration is given by the total charge, not the applied potential.

If we define a quantitative electrolysis as one in which we reduce 99.99% of $^{Cu2+}$ to Cu, then the concentration of Cu^{2+} at t_e is

$$[Cu^{2+}]_{t_e} = 0.0001 \times [Cu^{2+}]_0 \tag{11.3.6}$$

where $[Cu^{2+}]_0$ is the initial concentration of Cu^{2+} in the sample. Substituting Equation 11.3.6 into Equation 11.3.5 allows us to calculate the desired potential.

$$E = E^\circ_{Cu^{2+}/Cu} - \frac{0.05916}{2} \log \frac{1}{0.0001 \times [Cu^{2+}]}$$

If the initial concentration of Cu^{2+} is 1.00×10^{-4} M, for example, then the working electrode's potential must be more negative than +0.105 V to quantitatively reduce Cu^{2+} to Cu. Note that at this potential H_3O^+ is not reduced to H_2, maintaining 100% current efficiency.

Many controlled-potential coulometric methods for Cu^{2+} use a potential that is negative relative to the standard hydrogen electrode—see, for example, Rechnitz, G. A. *Controlled-Potential Analysis*, Macmillan: New York, 1963, p.49. Based on the ladder diagram in Figure 11.3.2 you might expect that applying a potential <0.000 V will partially reduce H_3O^+ to H_2, resulting in a current efficiency that is less than 100%. The reason we can use such a negative potential is that the reaction rate for the reduction of H_3O^+ to H_2 is very slow at a Pt electrode. This results in a significant ***overpotential***—the need to apply a potential more positive or a more negative than that predicted by thermodynamics—which shifts E^o for the H_3O^+/H_2 redox couple to a more negative value.

MINIMIZING ELECTROLYSIS TIME

In controlled-potential coulometry, as shown in Figure 11.3.1 , the current decreases over time. As a result, the rate of electrolysis—recall from Chapter 11.1 that current is a measure of rate—becomes slower and an exhaustive electrolysis of the analyte may require a long time. Because time is an important consideration when designing an analytical method, we need to consider the factors that affect the analysis time.

We can approximate the current's change as a function of time in Figure 11.3.1 as an exponential decay; thus, the current at time t is

$$i_t = i_0 e^{-kt} \tag{11.3.7}$$

where i_0 is the current at $t = 0$ and k is a rate constant that is directly proportional to the area of the working electrode and the rate of stirring, and that is inversely proportional to the volume of solution. For an exhaustive electrolysis in which we oxidize or reduce 99.99% of the analyte, the current at the end of the analysis, t_e, is

$$i_{t_e} \leq 0.0001 \times i_0 \tag{11.3.8}$$

Substituting Equation 11.3.8 into Equation 11.3.7 and solving for t_e gives the minimum time for an exhaustive electrolysis as

$$t_e = -\frac{1}{k} \times \ln(0.0001) = \frac{9.21}{k}$$

From this equation we see that a larger value for k reduces the analysis time. For this reason we usually carry out a controlled-potential coulometric analysis in a small volume electrochemical cell, using an electrode with a large surface area, and with a high stirring rate. A quantitative electrolysis typically requires approximately 30–60 min, although shorter or longer times are possible.

INSTRUMENTATION

A three-electrode potentiostat is used to set the potential in controlled-potential coulometry (see Figure 11.1.5). The working electrodes is usually one of two types: a cylindrical Pt electrode manufactured from platinum-gauze (Figure 11.3.3), or a Hg pool electrode. The large overpotential for the reduction of H_3O^+ at Hg makes it the electrode of choice for an analyte that requires a negative potential. For example, a potential more negative than –1 V versus the SHE is feasible at a Hg electrode—but not at a Pt electrode—even in a very acidic solution. Because mercury is easy to oxidize, it is less useful if we need to maintain a potential that is positive with respect to the SHE. Platinum is the working electrode of choice when we need to apply a positive potential.

Figure 11.3.3 . Example of a cylindrical Pt-gauze electrode used in controlled-potential coulometry. The electrode shown here has a diameter of 13 mm and a height of 48 mm, and was fashioned from Pt wire with a diameter of approximately 0.15 mm. The electrode's surface has 360 openings/cm^2 and a total surface area of approximately 40 cm^2.

The auxiliary electrode, which often is a Pt wire, is separated by a salt bridge from the analytical solution. This is necessary to prevent the electrolysis products generated at the auxiliary electrode from reacting with the analyte and interfering in the analysis. A saturated calomel or Ag/AgCl electrode serves as the reference electrode.

The other essential need for controlled-potential coulometry is a means for determining the total charge. One method is to monitor the current as a function of time and determine the area under the curve, as shown in Figure 11.3.1 . Modern instruments use electronic integration to monitor charge as a function of time. The total charge at the end of the electrolysis is read directly from a digital readout.

ELECTROGRAVIMETRY

If the product of controlled-potential coulometry forms a deposit on the working electrode, then we can use the change in the electrode's mass as the analytical signal. For example, if we apply a potential that reduces Cu^{2+} to Cu at a Pt working electrode, the difference in the electrode's mass before and after electrolysis is a direct measurement of the amount of copper in the sample. As we learned in Chapter 8, we call an analytical technique that uses mass as a signal a gravimetric technique; thus, we call this ***electrogravimetry***.

CONTROLLED-CURRENT COULOMETRY

A second approach to coulometry is to use a constant current in place of a constant potential, which results in the current-versus-time profile shown in Figure 11.3.4 . Controlled-current coulometry has two advantages over controlled-potential coulometry. First, the analysis time is shorter because the current does not decrease over time. A typical analysis time for controlled-current coulometry is less than 10 min, compared to approximately 30–60 min for controlled-potential coulometry. Second, because the total charge simply is the product of current and time (Equation **11.3.2**), there is no need to integrate the current-time curve in Figure 11.3.4 .

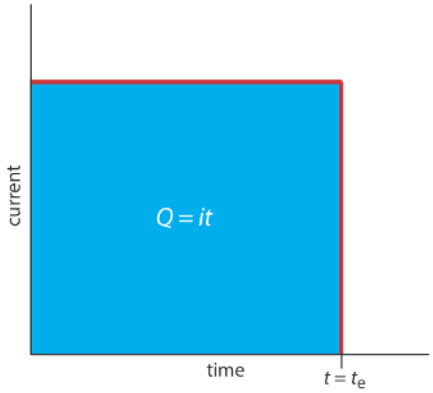


Figure 11.3.4 . Current versus time for a controlled-current coulometric analysis. The measured current is shown by the red curve. The integrated area under the curve, shown in blue, is the total charge.

Using a constant current presents us with two important experimental problems. First, during electrolysis the analyte's concentration—and, therefore, the current that results from its oxidation or reduction—decreases continuously. To maintain a constant current we must allow the potential to change until another oxidation reaction or reduction reaction occurs at the working electrode. Unless we design the system carefully, this secondary reaction results in a current efficiency that is less than 100%. The second problem is that we need a method to determine when the analyte's electrolysis is complete. As shown in Figure 11.3.1 , in a controlled-potential coulometric analysis we know that electrolysis is complete when the current reaches zero, or when it reaches a constant background or residual current. In a controlled-current coulometric analysis, however, current continues to flow even when the analyte's electrolysis is complete. A suitable method for determining the reaction's endpoint, t_e, is needed.

MAINTAINING CURRENT EFFICIENCY

To illustrate why a change in the working electrode's potential may result in a current efficiency of less than 100%, let's consider the coulometric analysis for Fe^{2+} based on its oxidation to Fe^{3+} at a Pt working electrode in 1 M H_2SO_4.

$$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$$

Figure 11.3.5 shows the ladder diagram for this system. At the beginning of the analysis, the potential of the working electrode remains nearly constant at a level near its initial value.

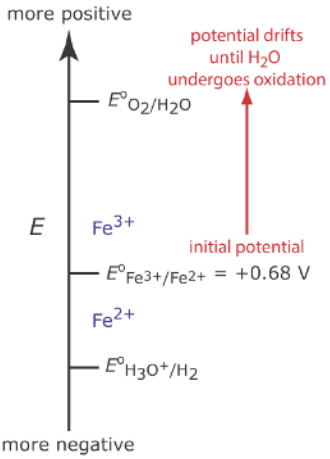


Figure 11.3.5 . Ladder diagram for the constant-current coulometric analysis of Fe^{2+}. The red arrow and text shows how the potential drifts to more positive values, decreasing the current efficiency.

As the concentration of Fe^{2+} decreases and the concentration of Fe^{3+} increases, the working electrode's potential shifts toward more positive values until the oxidation of H_2O begins.

$$2H_2O(l) \rightleftharpoons O_2(g) + 4H^+(aq) + 4e^-$$

Because a portion of the total current comes from the oxidation of H_2O, the current efficiency for the analysis is less than 100% and we cannot use Equation 11.3.1 to determine the amount of Fe^{2+} in the sample.

Although we cannot prevent the potential from drifting until another species undergoes oxidation, we can maintain a 100% current efficiency if the product of that secondary oxidation reaction both rapidly and quantitatively reacts with the remaining Fe^{2+}. To accomplish this we add an excess of Ce^{3+} to the analytical solution. As shown in Figure 11.3.6 , when the potential of the working electrode shifts to a more positive potential, Ce^{3+} begins to oxidize to Ce^{4+}

$$Ce^{3+}(aq) \rightleftharpoons Ce^{4+}(aq) + e^- \tag{11.3.9}$$

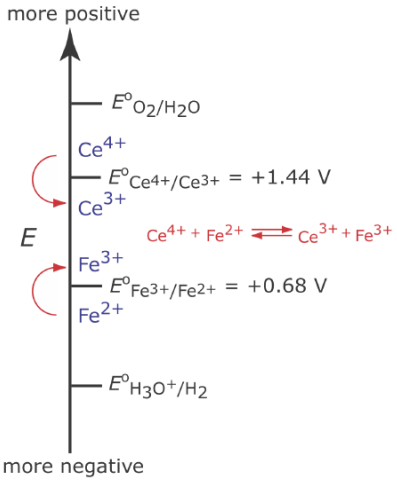


Figure 11.3.6 . Ladder diagram for the constant-current coulometric analysis of Fe^{2+} in the presence of a Ce^{3+} mediator. As the potential drifts to more positive values, we eventually reach a potential where Ce^{3+} undergoes oxidation. Because Ce^{4+}, the product of the oxidation of Ce^{3+}, reacts with Fe^{2+}, we maintain current efficiency.

The Ce^{4+} that forms at the working electrode rapidly mixes with the solution where it reacts with any available Fe^{2+}.

$$Ce^{4+}(aq) + Fe^{2+}(aq) \rightleftharpoons Ce^{3+}(aq) + Fe^{3+}(aq) \tag{11.3.10}$$

Combining reaction 11.3.9 and reaction 11.3.10 shows that the net reaction is the oxidation of Fe^{2+} to Fe^{3+}

$$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$$

which maintains a current efficiency of 100%. A species used to maintain 100% current efficiency is called a ***mediator***.

ENDPOINT DETERMINATION

Adding a mediator solves the problem of maintaining 100% current efficiency, but it does not solve the problem of determining when the analyte's electrolysis is complete. Using the analysis for Fe^{2+} in Figure 11.3.6 , when the oxidation of Fe^{2+} is complete current continues to flow from the oxidation of Ce^{3+}, and, eventually, the oxidation of H_2O. What we need is a signal that tells us when no more Fe^{2+} is present in the solution.

For our purposes, it is convenient to treat a controlled-current coulometric analysis as a reaction between the analyte, Fe^{2+}, and the mediator, Ce^{3+}, as shown by reaction 11.3.10. This reaction is identical to a redox titration; thus, we can use the end points for a redox titration—visual indicators and potentiometric or conductometric measurements—to signal the end of a controlled-current coulometric analysis. For example, ferroin provides a useful visual endpoint for the Ce^{3+} mediated coulometric analysis for Fe^{2+}, changing color from red to blue when the electrolysis of Fe^{2+} is complete.

> Reaction 11.3.10 is the same reaction we used in Chapter 9 to develop our understanding of redox titrimetry.

INSTRUMENTATION

Controlled-current coulometry normally is carried out using a two-electrode galvanostat, which consists of a working electrode and a counter electrode. The working electrode—often a simple Pt electrode—also is called the generator electrode since it is where the mediator reacts to generate the species that reacts with the analyte. If necessary, the counter electrode is isolated from the analytical solution by a salt bridge or a porous frit to prevent its electrolysis products from reacting with the analyte. Alternatively, we can generate the oxidizing agent or the reducing agent externally, and allow it to flow into the analytical solution. Figure 11.3.7 shows one simple method for accomplishing this. A solution that contains the mediator flows into a small-volume electrochemical cell with the products exiting through separate tubes. Depending upon the analyte, the oxidizing agent or the reducing reagent is delivered to the analytical solution. For example, we can generate Ce^{4+} using an aqueous solution of Ce^{3+}, directing the Ce^{4+} that forms at the anode to our sample.

Figure 11.1.4 shows an example of a manual galvanostat. Although a modern galvanostat uses very different circuitry, you can use Figure 11.1.4 and the accompanying discussion to understand how we can use the working electrode and the counter electrode to control the current. Figure 11.1.4 includes an optional reference electrode, but its presence or absence is not important if we are not interested in monitoring the working electrode's potential.

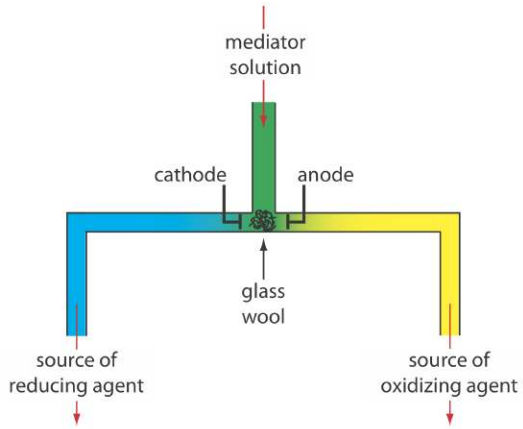


Figure 11.3.7 . One example of a device for the external generation of oxidizing agents and reducing agents for controlled-current coulometry. A solution containing the mediator flows into a small-volume electrochemical cell. The resulting oxidation products, which form at the anode, flow to the right and serve as an oxidizing agent. Reduction at the cathode generates a reducing agent.

There are two other crucial needs for controlled-current coulometry: an accurate clock for measuring the electrolysis time, t_e, and a switch for starting and stopping the electrolysis. An analog clock can record time to the nearest ±0.01 s, but the need to stop and start the electrolysis as we approach the endpoint may result in an overall uncertainty of ±0.1 s. A digital clock allows for a more accurate measurement of time, with an overall uncertainty of ±1 ms. The switch must control both the current and the clock so that we can make an accurate determination of the electrolysis time.

COULOMETRIC TITRATIONS

A controlled-current coulometric method sometimes is called a coulometric titration because of its similarity to a conventional titration. For example, in the controlled-current coulometric analysis for Fe^{2+} using a Ce^{3+} mediator, the oxidation of Fe^{2+} by Ce^{4+} (reaction 11.3.10) is identical to the reaction in a redox titration.

There are other similarities between controlled-current coulometry and titrimetry. If we combine Equation 11.3.1 and Equation 11.3.2 and solve for the moles of analyte, N_A, we obtain the following equation.

$$N_A = \frac{i}{nF} \times t_e \tag{11.3.11}$$

Compare Equation 11.3.11 to the relationship between the moles of analyte, N_A, and the moles of titrant, N_T, in a titration

$$N_A = N_T = M_T \times V_T$$

where M_T and V_T are the titrant's molarity and the volume of titrant at the end point. In constant-current coulometry, the current source is equivalent to the titrant and the value of that current is analogous to the titrant's molarity. Electrolysis time is analogous to the volume of titrant, and t_e is equivalent to the a titration's end point. Finally, the switch for starting and stopping the electrolysis serves the same function as a buret's stopcock.

For simplicity, we assumed above that the stoichiometry between the analyte and titrant is 1:1. The assumption, however, is not important and does not effect our observation of the similarity between controlled-current coulometry and a titration.

QUANTITATIVE APPLICATIONS

Coulometry is used for the quantitative analysis of both inorganic and organic analytes. Examples of controlled-potential and controlled-current coulometric methods are discussed in the following two sections.

CONTROLLED-POTENTIAL COULOMETRY

The majority of controlled-potential coulometric analyses involve the determination of inorganic cations and anions, including trace metals and halides ions. Table 11.3.1 summarizes several of these methods.

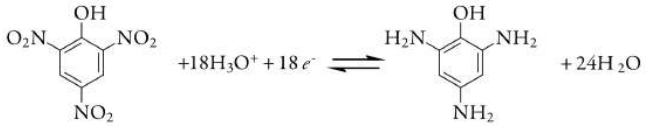
Table 11.3.1 . Representative Controlled-Potential Coulometric Analyses for Inorganic Ions

analyte	electrolytic reaction	electrode
antimony	$Sb(III) + 3e^- \rightleftharpoons Sb$	Pt
arsenic	$As(III) \rightleftharpoons As(V) + 2e^-$	Pt
cadmium	$Cd(II) + 2e^- \rightleftharpoons Cd$	Pt or Hg
cobalt	$Co(II) + 2e^- \rightleftharpoons Co$	Pt or Hg
copper	$Cu(II) + 2e^- \rightleftharpoons Cu$	Pt or Hg
halides (X^-)	$Ag + X^- \rightleftharpoons AgX + e^-$	Ag
iron	$Fe(II) \rightleftharpoons Fe(III) + e^-$	Pt
lead	$Pb(II) + 2e^- \rightleftharpoons Pb$	Pt or Hg
nickel	$Ni(II) + 2e^- \rightleftharpoons Ni$	Pt or Hg
plutonium	$Pu(III) \rightleftharpoons Pu(IV) + e^-$	Pt
silver	$Ag(I) + 1e^- \rightleftharpoons Ag$	Pt
tin	$Sn(II) + 2e^- \rightleftharpoons Sn$	Pt
uranium	$U(VI) + 2e^- \rightleftharpoons U(IV)$	Pt or Hg
zinc	$Zn(II) + 2e^- \rightleftharpoons Zn$	Pt or Hg

Source: Rechnitz, G. A. *Controlled-Potential Analysis*, Macmillan: New York, 1963.
Electrolytic reactions are written in terms of the change in the analyte's oxidation state. The actual species in solution depends on the analyte.

The ability to control selectivity by adjusting the working electrode's potential makes controlled-potential coulometry particularly useful for the analysis of alloys. For example, we can determine the composition of an alloy that contains Ag, Bi, Cd, and Sb by dissolving the sample and placing it in a matrix of 0.2 M H_2SO_4 along with a Pt working electrode and a Pt counter electrode. If we apply a constant potential of +0.40 V versus the SCE, Ag(I) deposits on the electrode as Ag and the other metal ions remain in solution. When electrolysis is complete, we use the total charge to determine the amount of silver in the alloy. Next, we shift the working electrode's potential to –0.08 V versus the SCE, depositing Bi on the working electrode. When the coulometric analysis for bismuth is complete, we determine antimony by shifting the working electrode's potential to –0.33 V versus the SCE, depositing Sb. Finally, we determine cadmium following its electrodeposition on the working electrode at a potential of –0.80 V versus the SCE.

We also can use controlled-potential coulometry for the quantitative analysis of organic compounds, although the number of applications is significantly less than that for inorganic analytes. One example is the six-electron reduction of a nitro group, $–NO_2$, to a primary amine, $–NH_2$, at a mercury electrode. Solutions of picric acid—also known as 2,4,6-trinitrophenol, or TNP, a close relative of TNT—is analyzed by reducing it to triaminophenol.



Another example is the successive reduction of trichloroacetate to dichloroacetate, and of dichloroacetate to monochloroacetate

$$Cl_3CCOO^-(aq) + H_3O^+(aq) + 2e^- \rightleftharpoons Cl_2HCCOO^-(aq) + Cl^-(aq) + H_2O(l)$$

$$Cl_2HCCOO^-(aq) + H_3O^+(aq) + 2e^- \rightleftharpoons ClH_2CCOO^-(aq) + Cl^-(aq) + H_2O(l)$$

We can analyze a mixture of trichloroacetate and dichloroacetate by selecting an initial potential where only the more easily reduced trichloroacetate reacts. When its electrolysis is complete, we can reduce dichloroacetate by adjusting the potential to a more negative

potential. The total charge for the first electrolysis gives the amount of trichloroacetate, and the difference in total charge between the first electrolysis and the second electrolysis gives the amount of dichloroacetate.

CONTROLLED-CURRENT COULOMETRY (COULOMETRIC TITRATIONS)

The use of a mediator makes a coulometric titration a more versatile analytical technique than controlled-potential coulometry. For example, the direct oxidation or reduction of a protein at a working electrode is difficult if the protein's active redox site lies deep within its structure. A coulometric titration of the protein is possible, however, if we use the oxidation or reduction of a mediator to produce a solution species that reacts with the protein. Table 11.3.2 summarizes several controlled-current coulometric methods based on a redox reaction using a mediator.

Table 11.3.2 . Representative Examples of Coulometric Redox Titrations

mediator	electrochemically generated reagent and reaction	representative application
Ag^+	$\mathbf{Ag^+ \rightleftharpoons Ag^{2+} + e^-}$	$\mathbf{H_2C_2O_4}(aq) + 2\mathbf{Ag^{2+}}(aq) + 2\mathbf{H_2O}(l) \rightleftharpoons 2\mathbf{CO_2}(g) + 2\mathbf{Ag^+}(aq) + 2\mathbf{H_3O^+}(aq)$
Br^-	$\mathbf{2Br^- \rightleftharpoons Br_2 + 2e^-}$	$\mathbf{H_2S}(aq) + \mathbf{Br_2}(aq) + 2\mathbf{H_2O}(l) \rightleftharpoons \mathbf{S}(s) + 2\mathbf{Br^-}(aq) + 2\mathbf{H_3O^+}(aq)$
Ce^{3+}	$\mathbf{Ce^{3+} \rightleftharpoons Ce^{4+} + e^-}$	$\mathbf{Fe(CN)_6^{4-}}(aq) + \mathbf{Ce^{4+}}(aq) \rightleftharpoons \mathbf{Fe(CN)_6^{3-}}(aq) + \mathbf{Ce^{3+}}(aq)$
Cl^-	$\mathbf{2Cl^- \rightleftharpoons Cl_2 + 2e^-}$	$\mathbf{Ti(I)}(aq) + \mathbf{Cl_2}(aq) \rightleftharpoons \mathbf{Ti(III)}(aq) + 2\mathbf{Cl^-}(aq)$
Fe^{3+}	$\mathbf{Fe^{3+}} + e^- \rightleftharpoons \mathbf{Fe^{2+}}$	$\mathbf{Cr_2O_7^{2-}}(aq) + 6\mathbf{Fe^{2+}}(aq) + 14\mathbf{H_3O^+}(aq) \rightleftharpoons 2\mathbf{Cr^{3+}}(aq) + 6\mathbf{Fe^{3+}}(aq) + 21\mathbf{H_2O}(l)$
I^-	$\mathbf{3I^- \rightleftharpoons I_3^-} + 2e^-$	$2\mathbf{S_2O_3^{2-}}(aq) + \mathbf{I_3^-}(aq) \rightleftharpoons \mathbf{S_4O_6^{2-}}(aq) + 3\mathbf{I^-}(aq)$
Mn^{2+}	$\mathbf{Mn^{2+} \rightleftharpoons Mn^{3+} + e^-}$	$\mathbf{As(III)}(aq) + 2\mathbf{Mn^{3+}}(aq) \rightleftharpoons \mathbf{As(V)}(aq) + 2\mathbf{Mn^{2+}}(aq)$

Note: The electrochemically generated reagent and the analyte are shown in **bold**.

For an analyte that is not easy to oxidize or reduce, we can complete a coulometric titration by coupling a mediator's oxidation or reduction to an acid–base, precipitation, or complexation reaction that involves the analyte. For example, if we use H_2O as a mediator, we can generate H_3O^+at the anode

$$\mathbf{6H_2O}(l) \rightleftharpoons \mathbf{4H_3O^+}(aq) + \mathbf{O_2}(g) + 4e^-$$

and generate OH^- at the cathode.

$$\mathbf{2H_2O}(l) + 2e^- \rightleftharpoons \mathbf{2OH^-}(aq) + \mathbf{H_2}(g)$$

If we carry out the oxidation or reduction of H_2O using the generator cell in Figure 11.3.7 , then we can selectively dispense H_3O^+ or OH^- into a solution that contains the analyte. The resulting reaction is identical to that in an acid–base titration. Coulometric acid–base titrations have been used for the analysis of strong and weak acids and bases, in both aqueous and non-aqueous matrices. Table 11.3.3 summarizes several examples of coulometric titrations that involve acid–base, complexation, and precipitation reactions.

Table 11.3.3 . Representative Coulometric Titrations Using Acid–Base, Complexation, and Precipitation Reactions

type of reaction	mediator	electrochemically generated reagent and reaction	representative application
acid-base	H_2O	$\mathbf{6H_2O} \rightleftharpoons \mathbf{4H_3O^+} + \mathbf{O_2} + e^-$	$\mathbf{OH^-}(aq) + \mathbf{H_3O^+}(aq) \rightleftharpoons 2\mathbf{H_2O}(l)$
acid-base	H_2O	$2\mathbf{H_2O} + 2e^- \rightleftharpoons 2\mathbf{OH^-} + \mathbf{H_2}$	$\mathbf{H_3O^+}(aq) + \mathbf{OH^-}(aq) \rightleftharpoons 2\mathbf{H_2O}(l)$
complexation	$HgNH_3Y^{2-}$ (Y = EDTA)	$\mathbf{HgNH_3Y^{2-}} + \mathbf{NH_4^+} + 2e^- \rightleftharpoons \mathbf{HY^{3-}} + \mathbf{Hg} + 2\mathbf{NH_3}$	$\mathbf{Ca^{2+}}(aq) + \mathbf{HY^{3-}}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{CaY^{2-}}(aq) + \mathbf{H_3O^+}(aq)$
complexation	Ag	$\mathbf{Ag} \rightleftharpoons \mathbf{Ag^+} + e^-$	$\mathbf{I^-}(aq) + \mathbf{Ag^+}(aq) \rightleftharpoons \mathbf{AgI}(s)$
precipitation	Hg	$2\mathbf{Hg} \rightleftharpoons \mathbf{Hg_2^{2+}} + 2e^-$	$2\mathbf{Cl^-}(aq) + \mathbf{Hg_2^{2+}}(aq) \rightleftharpoons \mathbf{Hg_2Cl_2}(s)$
precipitation	$Fe(CN)_6^{3-}$	$\mathbf{Fe(CN)_6^{3-}} + e^- \rightleftharpoons \mathbf{Fe(CN)_6^{4-}}$	$3\mathbf{Zn^{2+}}(aq) + \mathbf{K^+}(aq) + 2\mathbf{Fe(CN)_6^{4-}}(aq) \rightleftharpoons \mathbf{K_2Zn_3[Fe(CN)_6]_2}(s)$

Note: The electrochemically generated reagent and the analyte are shown in **bold**.

In comparison to a conventional titration, a coulometric titration has two important advantages. The first advantage is that electrochemically generating a titrant allows us to use a reagent that is unstable. Although we cannot prepare and store a solution of a highly reactive reagent, such as Ag^{2+} or Mn^{3+}, we can generate them electrochemically and use them in a coulometric titration. Second, because it is relatively easy to measure a small quantity of charge, we can use a coulometric titration to determine an analyte whose concentration is too small for a conventional titration.

QUANTITATIVE CALCULATIONS

The absolute amount of analyte in a coulometric analysis is determined using Faraday's law (Equation 11.3.1) and the total charge given by Equation 11.3.2 or by Equation 11.3.3. The following example shows the calculations for a typical coulometric analysis.

EXAMPLE 11.3.1

To determine the purity of a sample of $Na_2S_2O_3$, a sample is titrated coulometrically using I^- as a mediator and I_3^- as the titrant. A sample weighing 0.1342 g is transferred to a 100-mL volumetric flask and diluted to volume with distilled water. A 10.00-mL portion is transferred to an electrochemical cell along with 25 mL of 1 M KI, 75 mL of a pH 7.0 phosphate buffer, and several drops of a starch indicator solution. Electrolysis at a constant current of 36.45 mA requires 221.8 s to reach the starch indicator endpoint. Determine the sample's purity.

Solution

As shown in Table 11.3.2 , the coulometric titration of $S_2O_3^{2-}$ with I_3^- is

$$2S_2O_3^{2-}(aq) + I_3^-(aq) \rightleftharpoons S_4O_6^{2-}(aq) + 3I^-(aq)$$

The oxidation of $S_2O_3^{2-}$ to $S_4O_6^{2-}$ requires one electron per $S_2O_3^{2-}$ (n = 1). Combining Equation 11.3.1 and Equation 11.3.2, and solving for the moles and grams of $Na_2S_2O_3$ gives

$$N_A = \frac{it_e}{nF} = \frac{(0.03645\text{ A})(221.8\text{ s})}{\left(\frac{1\text{ mol }e^-}{\text{mol }Na_2S_2O_3}\right)\left(\frac{96487\text{ C}}{\text{mol }e^-}\right)} = 8.379 \times 10^{-5}\text{ mol }Na_2S_2O_3$$

This is the amount of $Na_2S_2O_3$ in a 10.00-mL portion of a 100-mL sample; thus, there are 0.1325 grams of $Na_2S_2O_3$ in the original sample. The sample's purity, therefore, is

$$\frac{0.1325\text{ g }Na_2S_2O_3}{0.1342\text{ g sample}} \times 100 = 98.73\%\text{ w/w }Na_2S_2O_3$$

Note that for Equation 11.3.1 and Equation 11.3.2 it does not matter whether $S_2O_3^{2-}$ is oxidized at the working electrode or is oxidized by I_3^-.

EXERCISE 11.3.1

To analyze a brass alloy, a 0.442-g sample is dissolved in acid and diluted to volume in a 500-mL volumetric flask. Electrolysis of a 10.00-mL sample at –0.3 V versus a SCE reduces Cu^{2+} to Cu, requiring a total charge of 16.11 C. Adjusting the potential to –0.6 V versus a SCE and completing the electrolysis requires 0.442 C to reduce Pb^{2+} to Pb. Report the %w/w Cu and Pb in the alloy.

Answer

The reduction of Cu^{2+} to Cu requires two electrons per mole of Cu (n = 2). Using Equation 11.3.1, we calculate the moles and the grams of Cu in the portion of sample being analyzed.

$$N_{Cu} = \frac{Q}{nF} = \frac{16.11\text{ C}}{\frac{2\text{ mol }e^-}{\text{mol Cu}} \times \frac{96487\text{ C}}{\text{mol }e^-}} = 8.348 \times 10^{-5}\text{ mol Cu}$$

$$8.348 \times 10^{-5}\text{ mol Cu} \times \frac{63.55\text{ g Cu}}{\text{mol Cu}} = 5.301 \times 10^{-3}\text{ g Cu}$$

This is the Cu from a 10.00 mL portion of a 500.0 mL sample; thus, the %/w/w copper in the original sample of brass is

$$\frac{5.301 \times 10^{-3}\text{ g Cu} \times \frac{500.0\text{ mL}}{10.00\text{ mL}}}{0.442\text{ g sample}} \times 100 = 60.0\%\text{ w/w Cu}$$

For lead, we follow the same process; thus

$$N_{Pb} = \frac{Q}{nF} = \frac{0.422\text{ C}}{\frac{2\text{ mol }e^-}{\text{mol Pb}} \times \frac{96487\text{ C}}{\text{mol }e^-}} = 2.19 \times 10^{-6}\text{ mol Pb}$$

$$2.19 \times 10^{-6}\text{ mol Pb} \times \frac{207.2\text{ g Pb}}{\text{mol Cu}} = 4.53 \times 10^{-4}\text{ g Pb}$$

$$\frac{4.53 \times 10^{-4}\text{ g Pb} \times \frac{500.0\text{ mL}}{10.00\text{ mL}}}{0.442\text{ g sample}} \times 100 = 5.12\%\text{ w/w Pb}$$

REPRESENTATIVE METHOD 11.3.1: DETERMINATION OF DICHROMATE BY A COULOMETRIC REDOX TITRATION

The best way to appreciate the theoretical and the practical details discussed in this section is to carefully examine a typical analytical method. Although each method is unique, the following description of the determination of $Cr_2O_7^{2-}$ provides an instructive example of a typical procedure. The description here is based on Bassett, J.; Denney, R. C.; Jeffery, G. H.; Mendham, J. *Vogel's Textbook of Quantitative Inorganic Analysis*, Longman: London, 1978, p. 559–560.

Description of the Method

Thee concentration of $Cr_2O_7^{2-}$ in a sample is determined by a coulometric redox titration using Fe^{3+} as a mediator and electrogenerated Fe^{3+} as the titrant. The endpoint of the titration is determined potentiometrically.

Procedure

The electrochemical cell consists of a Pt working electrode and a Pt counter electrode placed in separate cells connected by a porous glass disk. Fill the counter electrode's cell with 0.2 M Na_2SO_4, keeping the level above that of the solution in the working electrode's cell. Connect a platinum electrode and a tungsten electrode to a potentiometer so that you can measure the working electrode's potential during the analysis. Prepare a mediator solution of approximately 0.3 M $NH_4Fe(SO_4)_2$. Add 5.00 mL of sample, 2 mL of 9 M H_2SO_4, and 10–25 mL of the mediator solution to the working electrode's cell, and add distilled water as needed to cover the electrodes. Bubble pure N_2 through the solution for 15 min to remove any O_2 that is present. Maintain the flow of N_2 during the electrolysis, turning if off momentarily when measuring the potential. Stir the solution using a magnetic stir bar. Adjust the current to 15–50 mA and begin the titration. Periodically stop the titration and measure the potential. Construct a titration curve of potential versus time and determine the time needed to reach the equivalence point.

Questions

1. Is the platinum working electrode the cathode or the anode?

Reduction of Fe^{3+} to Fe^{2+} occurs at the working electrode, making it the cathode in this electrochemical cell.

2. Why is it necessary to remove dissolved oxygen by bubbling N_2 through the solution?

Any dissolved O_2 will oxidize Fe^{2+} back to Fe^{3+}, as shown by the following reaction.

$$4Fe^{2+}(aq) + O_2 + 4H_3O^+(aq) \rightleftharpoons 4Fe^{3+}(aq) + 6H_2O(l)$$

To maintain current efficiency, all the Fe^{2+} must react with $Cr_2O_7^{2-}$. The reaction of Fe^{2+} with O_2 means that more of the Fe^{3+} mediator is needed, increasing the time to reach the titration's endpoint. As a result, we report the presence of too much $Cr_2O_7^{2-}$.

3. What is the effect on the analysis if the $NH_4Fe(SO_4)_2$ is contaminated with trace amounts of Fe^{2+}? How can you compensate for this source of Fe^{2+}?

There are two sources of Fe^{2+}: that generated from the mediator and that present as an impurity. Because the total amount of Fe^{2+} that reacts with $Cr_2O_7^{2-}$ remains unchanged, less Fe^{2+} is needed from the mediator. This decreases the time needed to reach the titration's end point. Because the apparent current efficiency is greater than 100%, the reported concentration of $Cr_2O_7^{2-}$ is too small. We can remove trace amount of Fe^{2+} from the mediator's solution by adding H_2O_2 and heating at 50–70°C until the evolution of O_2 ceases, converting the Fe^{2+} to Fe^{3+}. Alternatively, we can complete a blank titration to correct for any impurities of Fe^{2+} in the mediator.

4. Why is the level of solution in the counter electrode's cell maintained above the solution level in the working electrode's cell?

This prevents the solution that contains the analyte from entering the counter electrode's cell. The oxidation of H_2O at the counter electrode produces O_2, which can react with the Fe^{2+} generated at the working electrode or the Cr^{3+} resulting from the reaction of Fe^{2+} and $Cr_2O_7^{2-}$. In either case, the result is a positive determinate error.

CHARACTERIZATION APPLICATIONS

One useful application of coulometry is determining the number of electrons involved in a redox reaction. To make the determination, we complete a controlled-potential coulometric analysis using a known amount of a pure compound. The total charge at the end of the electrolysis is used to determine the value of *n* using Faraday's law (Equation 11.3.1).

✔ EXAMPLE 11.3.2

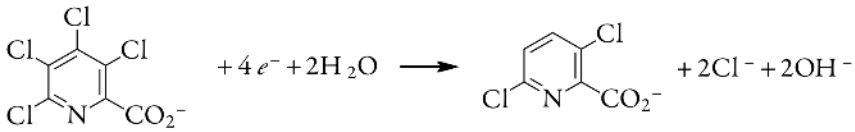
A 0.3619-g sample of tetrachloropicolinic acid, $C_6HNO_2Cl_4$, is dissolved in distilled water, transferred to a 1000-mL volumetric flask, and diluted to volume. An exhaustive controlled-potential electrolysis of a 10.00-mL portion of this solution at a spongy silver cathode requires 5.374 C of charge. What is the value of *n* for this reduction reaction?

Solution

The 10.00-mL portion of sample contains 3.619 mg, or 1.39×10^{-5} mol of tetrachloropicolinic acid. Solving Equation 11.3.1 for n and making appropriate substitutions gives

$$n = \frac{Q}{FN_A} = \frac{5.374\ \text{C}}{(96478\ \text{C/mol}\ e^-)\,(1.39 \times 10^{-5}\ \text{mol}\ C_6HNO_2Cl_4)} = 4.01\ \text{mol}\ e^-/\text{mol}\ C_6HNO_2Cl_4$$

Thus, reducing a molecule of tetrachloropicolinic acid requires four electrons. The overall reaction, which results in the selective formation of 3,6-dichloropicolinic acid, is



EVALUATION

SCALE OF OPERATION

A coulometric method of analysis can analyze a small absolute amount of an analyte. In controlled-current coulometry, for example, the moles of analyte consumed during an exhaustive electrolysis is given by Equation 11.3.11. An electrolysis using a constant current of 100 μA for 100 s, for example, consumes only 1×10^{-7} mol of analyte if n = 1. For an analyte with a molecular weight of 100 g/mol, 1×10^{-7} mol of analyte corresponds to only 10 μg. The concentration of analyte in the electrochemical cell, however, must be sufficient to allow an accurate determination of the endpoint. When using a visual end point, the smallest concentration of analyte that can be determined by a coulometric titration is approximately 10^{-4} M. As is the case for a conventional titration, a coulometric titration using a visual end point is limited to major and minor analytes. A coulometric titration to a preset potentiometric endpoint is feasible even if the analyte's concentration is as small as 10^{-7} M, extending the analysis to trace analytes [Curran, D. J. "Constant-Current Coulometry," in Kissinger, P. T.; Heineman, W. R., eds., *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker Inc.: New York, 1984, pp. 539–568].

ACCURACY

In controlled-current coulometry, accuracy is determined by the accuracy with which we can measure current and time, and by the accuracy with which we can identify the end point. The maximum measurement errors for current and time are about ±0.01% and ±0.1%, respectively. The maximum end point error for a coulometric titration is at least as good as that for a conventional titration, and is often better when using small quantities of reagents. Together, these measurement errors suggest that an accuracy of 0.1%–0.3% is feasible. The limiting factor in many analyses, therefore, is current efficiency. A current efficiency of more than 99.5% is fairly routine, and it often exceeds 99.9%.

In controlled-potential coulometry, accuracy is determined by current efficiency and by the determination of charge. If the sample is free of interferents that are easier to oxidize or reduce than the analyte, a current efficiency of greater than 99.9% is routine. When an interferent is present, it can often be eliminated by applying a potential where the exhaustive electrolysis of the interferents is possible without the simultaneous electrolysis of the analyte. Once the interferent is removed the potential is switched to a level where electrolysis of the analyte is feasible. The limiting factor in the accuracy of many controlled-potential coulometric methods of analysis is the determination of charge. With electronic integrators the total charge is determined with an accuracy of better than 0.5%.

If we cannot obtain an acceptable current efficiency, an electrogravimetric analysis is possible if the analyte—and only the analyte—forms a solid deposit on the working electrode. In this case the working electrode is weighed before beginning the electrolysis and reweighed when the electrolysis is complete. The difference in the electrode's weight gives the analyte's mass.

PRECISION

Precision is determined by the uncertainties in measuring current, time, and the endpoint in controlled-current coulometry or the charge in controlled-potential coulometry. Precisions of ±0.1–0.3% are obtained routinely in coulometric titrations, and precisions of ±0.5% are typical for controlled-potential coulometry.

SENSITIVITY

For a coulometric method of analysis, the calibration sensitivity is equivalent to nF in Equation 11.3.1. In general, a coulometric method is more sensitive if the analyte's oxidation or reduction involves a larger value of n.

SELECTIVITY

Selectivity in controlled-potential and controlled-current coulometry is improved by adjusting solution conditions and by selecting the electrolysis potential. In controlled-potential coulometry, the potential is fixed by the potentiostat, and in controlled-current coulometry the potential is determined by the redox reaction with the mediator. In either case, the ability to control the electrolysis potential affords some measure of selectivity. By adjusting pH or by adding a complexing agent, it is possible to shift the potential at which an analyte or interferent undergoes oxidation or reduction. For example, the standard-state reduction potential for Zn^{2+} is –0.762 V versus the SHE. If we add a solution of NH_3, forming $Zn(NH_3)_4^{2+}$, the standard state potential shifts to –1.04 V. This provides an additional means for controlling selectivity when an analyte and an interferent undergo electrolysis at similar potentials.

TIME, COST, AND EQUIPMENT

Controlled-potential coulometry is a relatively time consuming analysis, with a typical analysis requiring 30–60 min. Coulometric titrations, on the other hand, require only a few minutes, and are easy to adapt to an automated analysis. Commercial instrumentation for both controlled-potential and controlled-current coulometry is available, and is relatively inexpensive. Low cost potentiostats and constant-current sources are available for approximately $1000.

11.4: VOLTAMMETRIC AND AMPEROMETRIC METHODS

In ***voltammetry*** we apply a time-dependent potential to an electrochemical cell and measure the resulting current as a function of that potential. We call the resulting plot of current versus applied potential a ***voltammogram***, and it is the electrochemical equivalent of a spectrum in spectroscopy, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction [Maloy, J. T. *J. Chem. Educ.* **1983**, *60*, 285–289]. The earliest voltammetric technique is polarography, developed by Jaroslav Heyrovsky in the early 1920s—an achievement for which he was awarded the Nobel Prize in Chemistry in 1959. Since then, many different forms of voltammetry have been developed, a few of which are highlighted in Figure 11.1.6. Before examining these techniques and their applications in more detail, we must first consider the basic experimental design for voltammetry and the factors influencing the shape of the resulting voltammogram.

For an on-line introduction to much of the material in this section, see Analytical Electrochemistry: The Basic Concepts by Richard S. Kelly, a resource that is part of the Analytical Sciences Digital Library.

VOLTAMMETRIC MEASUREMENTS

Although early voltammetric methods used only two electrodes, a modern voltammeter makes use of a three-electrode potentiostat, such as that shown in Figure 11.1.5. In voltammetry we apply a time-dependent potential excitation signal to the working electrode—changing its potential relative to the fixed potential of the reference electrode—and measure the current that flows between the working electrode and the auxiliary electrode. The auxiliary electrode generally is a platinum wire and the reference electrode usually is a SCE or a Ag/AgCl electrode.

Figure 11.1.5 shows an example of a manual three-electrode potentiostat. Although a modern potentiostat uses very different circuitry, you can use Figure 11.1.5 and the accompanying discussion to understand how we can control the potential of working electrode and measure the resulting current.

For the working electrode we can choose among several different materials, including mercury, platinum, gold, silver, and carbon. The earliest voltammetric techniques used a mercury working electrode. Because mercury is a liquid, the working electrode usual is a drop suspended from the end of a capillary tube. In the ***hanging mercury drop electrode***, or HMDE, we extrude the drop of Hg by rotating a micrometer screw that pushes the mercury from a reservoir through a narrow capillary tube (Figure 11.4.1 a).

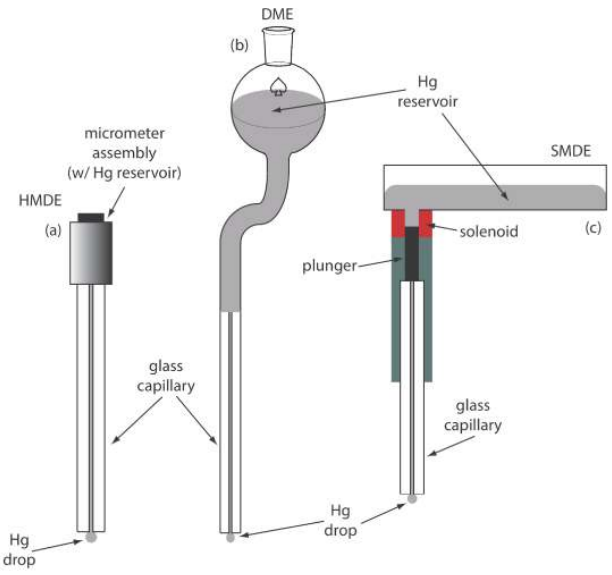


Figure 11.4.1 . Three examples of mercury electrodes: (a) hanging mercury drop electrode, or HMDE; (b) dropping mercury electrode, or DME; and (c) static mercury drop electrode, or SMDE.

In the ***dropping mercury electrode***, or DME, mercury drops form at the end of the capillary tube as a result of gravity (Figure 11.4.1 b). Unlike the HMDE, the mercury drop of a DME grows continuously—as mercury flows from the reservoir under the influence of gravity—and has a finite lifetime of several seconds. At the end of its lifetime the mercury drop is dislodged, either manually or on its own, and is replaced by a new drop. The ***static mercury drop electrode***, or SMDE, uses a solenoid driven plunger to control the flow of mercury (Figure

11.4.1 c). Activation of the solenoid momentarily lifts the plunger, allowing mercury to flow through the capillary, forming a single, hanging Hg drop. Repeated activation of the solenoid produces a series of Hg drops. In this way the SMDE may be used as either a HMDE or a DME. There is one additional type of mercury electrode: the ***mercury film electrode***. A solid electrode—typically carbon, platinum, or gold—is placed in a solution of Hg^{2+} and held at a potential where the reduction of Hg^{2+} to Hg is favorable, depositing a thin film of mercury on the solid electrode's surface.

Mercury has several advantages as a working electrode. Perhaps its most important advantage is its high overpotential for the reduction of H_3O^+ to H_2, which makes accessible potentials as negative as –1 V versus the SCE in acidic solutions and –2 V versus the SCE in basic solutions (Figure 11.4.2). A species such as Zn^{2+}, which is difficult to reduce at other electrodes without simultaneously reducing H_3O^+, is easy to reduce at a mercury working electrode. Other advantages include the ability of metals to dissolve in mercury—which results in the formation of an ***amalgam***—and the ability to renew the surface of the electrode by extruding a new drop. One limitation to mercury as a working electrode is the ease with which it is oxidized. Depending on the solvent, a mercury electrode can not be used at potentials more positive than approximately –0.3 V to +0.4 V versus the SCE.

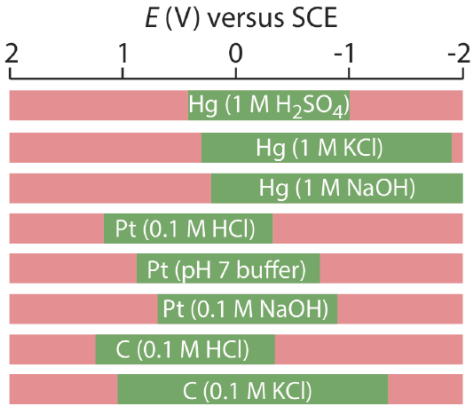


Figure 11.4.2 . Approximate potential windows for mercury, platinum, and carbon (graphite) electrodes in acidic, neutral, and basic aqueous solvents. The useful potential windows are shown in green; potentials in red result in the oxidation or the reduction of the solvent or the electrode. Complied from Adams, R. N. *Electrochemistry at Solid Electrodes*, Marcel Dekker, Inc.: New York, 1969 and Bard, A. J.; Faulkner, L. R. *Electro- chemical Methods*, John Wiley & Sons: New York, 1980.

Solid electrodes constructed using platinum, gold, silver, or carbon may be used over a range of potentials, including potentials that are negative and positive with respect to the SCE (Figure 11.4.2). For example, the potential window for a Pt electrode extends from approximately +1.2 V to –0.2 V versus the SCE in acidic solutions, and from +0.7 V to –1 V versus the SCE in basic solutions. A solid electrode can replace a mercury electrode for many voltammetric analyses that require negative potentials, and is the electrode of choice at more positive potentials. Except for the carbon paste electrode, a solid electrode is fashioned into a disk and sealed into the end of an inert support with an electrical lead (Figure 11.4.3). The carbon paste electrode is made by filling the cavity at the end of the inert support with a paste that consists of carbon particles and a viscous oil. Solid electrodes are not without problems, the most important of which is the ease with which the electrode's surface is altered by the adsorption of a solution species or by the formation of an oxide layer. For this reason a solid electrode needs frequent reconditioning, either by applying an appropriate potential or by polishing.

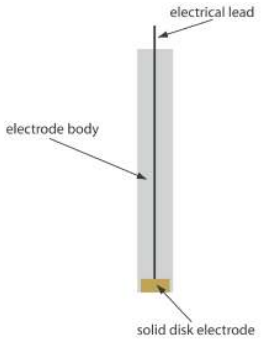


Figure 11.4.3 . Schematic showing a solid electrode. The electrode is fashioned into a disk and sealed in the end of an inert polymer support along with an electrical lead.

A typical arrangement for a voltammetric electrochemical cell is shown in Figure 11.4.4 . In addition to the working electrode, the reference electrode, and the auxiliary electrode, the cell also includes a N_2-purge line for removing dissolved O_2, and an optional stir bar.

Electrochemical cells are available in a variety of sizes, allowing the analysis of solution volumes ranging from more than 100 mL to as small as 50 μL.

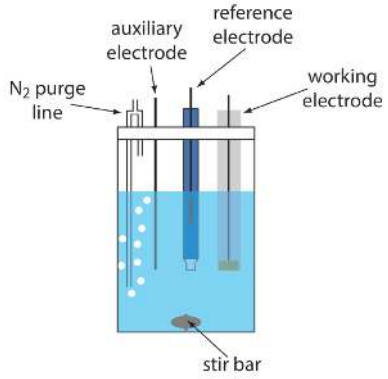


Figure 11.4.4 . Typical electrochemical cell for voltammetry.

CURRENT IN VOLTAMMETRY

When we oxidize an analyte at the working electrode, the resulting electrons pass through the potentiostat to the auxiliary electrode, reducing the solvent or some other component of the solution matrix. If we reduce the analyte at the working electrode, the current flows from the auxiliary electrode to the cathode. In either case, the current from the redox reactions at the working electrode and the auxiliary electrodes is called a ***faradaic current***. In this section we consider the factors affecting the magnitude of the faradaic current, as well as the sources of any non-faradaic currents.

SIGN CONVENTIONS

Because the reaction of interest occurs at the working electrode, we describe the faradaic current using this reaction. A faradaic current due to the analyte's reduction is a ***cathodic current***, and its sign is positive. An ***anodic current*** results from the analyte's oxidation at the working electrode, and its sign is negative.

INFLUENCE OF APPLIED POTENTIAL ON THE FARADAIC CURRENT

As an example, let's consider the faradaic current when we reduce $\mathbf{Fe(CN)_6^{3-}}$ to $\mathbf{Fe(CN)_6^{4-}}$ at the working electrode. The relationship between the concentrations of $\mathbf{Fe(CN)_6^{3-}}$, the concentration of $\mathbf{Fe(CN)_6^{4-}}$, and the potential is given by the Nernst equation

$$E = +0.356\ \text{V} - 0.05916 \log \frac{[\mathbf{Fe(CN)_6^{4-}}]_{x=0}}{[\mathbf{Fe(CN)_6^{3-}}]_{x=0}}$$

where +0.356V is the standard-statepotential for the $\mathbf{Fe(CN)_6^{3-}}$/$\mathbf{Fe(CN)_6^{4-}}$ redox couple, and x = 0 indicates that the concentrations of $\mathbf{Fe(CN)_6^{3-}}$- and $\mathbf{Fe(CN)_6^{4-}}$ are those at the surface of the working electrode. We use surface concentrations instead of bulk concentrations because the equilibrium position for the redox reaction

$$\mathbf{Fe(CN)_6^{3-}}(aq) + e^- \rightleftharpoons \mathbf{Fe(CN)_6^{4-}}(aq)$$

is established at the electrode's surface.

Let's assume we have a solution for which the initial concentration of $\mathbf{Fe(CN)_6^{3-}}$ is 1.0 mM and that $\mathbf{Fe(CN)_6^{4-}}$ is absent. Figure 11.4.5 shows the ladder diagram for this solution.

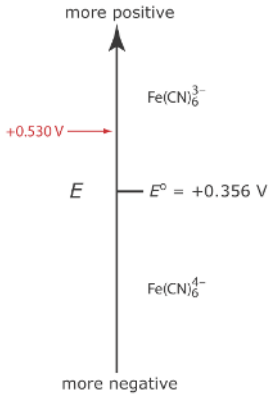


Figure 11.4.5 . Ladder diagram for the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox half-reaction.

If we apply a potential of +0.530 V to the working electrode, the concentrations of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ at the surface of the electrode are unaffected, and no faradaic current is observed. If we switch the potential to +0.356 V some of the $Fe(CN)_6^{3-}$ at the electrode's surface is reduced to $Fe(CN)_6^{4-}$until we reach a condition where

$$[Fe(CN)_6^{3-}]_{x=0} = [Fe(CN)_6^{4-}]_{x=0} = 0.50 \text{ mM}$$

This is the first of the five important principles of electrochemistry outlined in Chapter 11.1: the electrode's potential determines the analyte's form at the electrode's surface.

If this is all that happens after we apply the potential, then there would be a brief surge of faradaic current that quickly returns to zero, which is not the most interesting of results. Although the concentrations of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ at the electrode surface are 0.50 mM, their concentrations in bulk solution remains unchanged.

This is the second of the five important principles of electrochemistry outlined in Chapter 11.1: the analyte's concentration at the electrode may not be the same as its concentration in bulk solution.

Because of this difference in concentration, there is a concentration gradient between the solution at the electrode's surface and the bulk solution. This concentration gradient creates a driving force that transports $Fe(CN)_6^{4-}$ away from the electrode and that transports $Fe(CN)_6^{3-}$ to the electrode (Figure 11.4.6). As the $Fe(CN)_6^{3-}$ arrives at the electrode it, too, is reduced to $Fe(CN)_6^{4-}$. A faradaic current continues to flow until there is no difference between the concentrations of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ at the electrode and their concentrations in bulk solution.

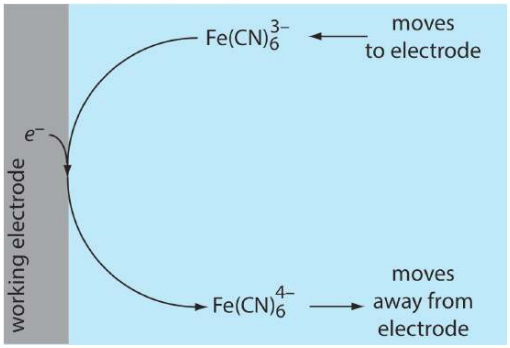


Figure 11.4.6 . Schematic diagram showing the transport of $Fe(CN)_6^{4-}$ away from the electrode's surface and the transport of $Fe(CN)_6^{3-}$ toward the electrode's surface following the reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$.

Although the potential at the working electrode determines if a faradaic current flows, the magnitude of the current is determined by the rate of the resulting oxidation or reduction reaction. Two factors contribute to the rate of the electrochemical reaction: the rate at which the reactants and products are transported to and from the electrode—what we call ***mass transport***—and the rate at which electrons pass between the electrode and the reactants and products in solution.

This is the fourth of the five important principles of electrochemistry outlined in Chapter 11.1: current is a measure of rate.

INFLUENCE OF MASS TRANSPORT ON THE FARADAIC CURRENT

There are three modes of mass transport that affect the rate at which reactants and products move toward or away from the electrode surface: diffusion, migration, and convection. ***Diffusion*** occurs whenever the concentration of an ion or a molecule at the surface of the electrode is different from that in bulk solution. If we apply a potential sufficient to completely reduce $\mathbf{Fe(CN)_6^{3-}}$ at the electrode surface, the result is a concentration gradient similar to that shown in Figure 11.4.7 . The region of solution over which diffusion occurs is the ***diffusion layer***. In the absence of other modes of mass transport, the width of the diffusion layer, δ, increases with time as the $\mathbf{Fe(CN)_6^{3-}}$ must diffuse from an increasingly greater distance.

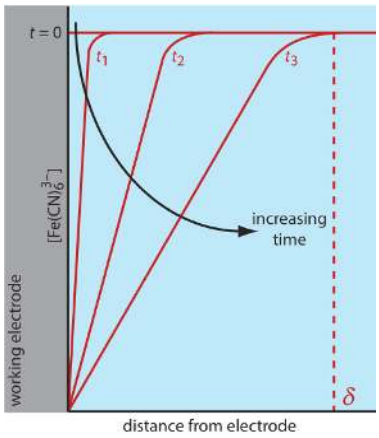


Figure 11.4.7 . Concentration gradients (in red) for $\mathbf{Fe(CN)_6^{3-}}$ following the application of a potential that completely reduces it to $\mathbf{Fe(CN)_6^{4-}}$. Before we apply the potential (t = 0) the concentration of $\mathbf{Fe(CN)_6^{3-}}$ is the same at all distances from the electrode's surface. After we apply the potential, its concentration at the electrode's surface decreases to zero and $\mathbf{Fe(CN)_6^{3-}}$ diffuses to the electrode from bulk solution. The longer we apply the potential, the greater the distance over which diffusion occurs. The dashed red line shows the extent of the diffusion layer at time t_3. These profiles assume that convection and migration do not contribute significantly to the mass transport of $\mathbf{Fe(CN)_6^{3-}}$.

Convection occurs when we mix the solution, which carries reactants toward the electrode and removes products from the electrode. The most common form of convection is stirring the solution with a stir bar; other methods include rotating the electrode and incorporating the electrode into a flow-cell.

The final mode of mass transport is ***migration***, which occurs when a charged particle in solution is attracted to or repelled from an electrode that carries a surface charge. If the electrode carries a positive charge, for example, an anion will move toward the electrode and a cation will move toward the bulk solution. Unlike diffusion and convection, migration affects only the mass transport of charged particles.

The movement of material to and from the electrode surface is a complex function of all three modes of mass transport. In the limit where diffusion is the only significant form of mass transport, the current in a voltammetric cell is equal to

$$i = \frac{nFAD\,(C_{\text{bulk}} - C_{x=0})}{\delta} \tag{11.4.1}$$

where n the number of electrons in the redox reaction, F is Faraday's constant, A is the area of the electrode, D is the diffusion coefficient for the species reacting at the electrode, C_{bulk} and $C_{x\,=\,0}$ are its concentrations in bulk solution and at the electrode surface, and δ is the thickness of the diffusion layer.

For Equation 11.4.1 to be valid, convection and migration must not interfere with the formation of a diffusion layer. We can eliminate migration by adding a high concentration of an inert supporting electrolyte. Because ions of similar charge equally are attracted to or repelled from the surface of the electrode, each has an equal probability of undergoing migration. A large excess of an inert electrolyte ensures that few reactants or products experience migration. Although it is easy to eliminate convection by not stirring the solution, there are experimental designs where we cannot avoid convection, either because we must stir the solution or because we are using an electrochemical flow cell. Fortunately, as shown in Figure 11.4.8 , the dynamics of a fluid moving past an electrode results in a small diffusion layer—typically 1–10 μm in thickness—in which the rate of mass transport by convection drops to zero.

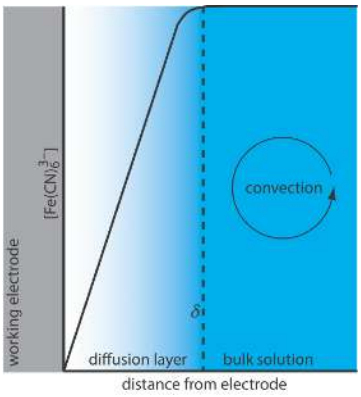


Figure 11.4.8 . Concentration gradient for $Fe(CN)_6^{3-}$ when stirring the solution. Diffusion is the only significant form of mass transport close to the electrode's surface. At distances greater than δ, convection is the only significant form of mass transport, maintaining a homogeneous solution in which the concentration of $Fe(CN)_6^{3-}$ at δ is the same as its concentration in bulk solution.

EFFECT OF ELECTRON TRANSFER KINETICS ON THE FARADAIC CURRENT

The rate of mass transport is one factor that influences the current in voltammetry. The ease with which electrons move between the electrode and the species that reacts at the electrode also affects the current. When electron transfer kinetics are fast, the redox reaction is at equilibrium. Under these conditions the redox reaction is ***electrochemically reversible*** and the Nernst equation applies. If the electron transfer kinetics are sufficiently slow, the concentration of reactants and products at the electrode surface—and thus the magnitude of the faradaic current—are not what is predicted by the Nernst equation. In this case the system is ***electrochemically irreversible***.

CHARGING CURRENTS

In addition to the faradaic current from a redox reaction, the current in an electrochemical cell includes other, nonfaradaic sources. Suppose the charge on an electrode is zero and we suddenly change its potential so that the electrode's surface acquires a positive charge. Cations near the electrode's surface will respond to this positive charge by migrating away from the electrode; anions, on the other hand, will migrate toward the electrode. This migration of ions occurs until the electrode's positive surface charge and the negative charge of the solution near the electrode are equal. Because the movement of ions and the movement of electrons are indistinguishable, the result is a small, short-lived ***nonfaradaic current*** that we call the ***charging current***. Every time we change the electrode's potential, a transient charging current flows.

> The migration of ions in response to the electrode's surface charge leads to the formation of a structured electrode-solution interface that we call the ***electrical double layer***, or EDL. When we change an electrode's potential, the charging current is the result of a restructuring of the EDL. The exact structure of the electrical double layer is not important in the context of this text, but you can consult this chapter's additional resources for additional information.

RESIDUAL CURRENT

Even in the absence of analyte, a small, measurable current flows through an electrochemical cell. This ***residual current*** has two components: a faradaic current due to the oxidation or reduction of trace impurities and a nonfaradaic charging current. Methods for discriminating between the analyte's faradaic current and the residual current are discussed later in this chapter.

SHAPE OF VOLTAMMOGRAMS

The shape of a voltammogram is determined by several experimental factors, the most important of which are how we measure the current and whether convection is included as a means of mass transport. As shown in Figure 11.4.9 , despite an abundance of different voltammetric techniques, several of which are discussed in this chapter, there are only three common shapes for voltammograms.

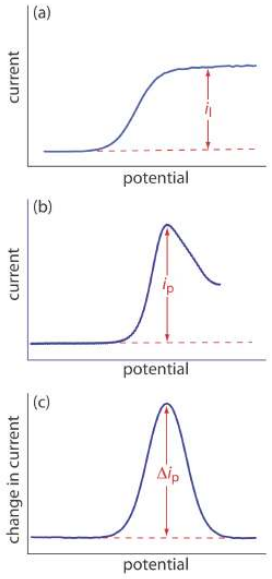


Figure 11.4.9 . The three common shapes for voltammograms. The dashed red line shows the residual current.

For the voltammogram in Figure 11.4.9 a, the current increases from a background residual current to a ***limiting current***, i_l. Because the faradaic current is inversely proportional to δ (Equation 11.4.1), a limiting current occurs only if the thickness of the diffusion layer remains constant because we are stirring the solution (see Figure 11.4.8). In the absence of convection the diffusion layer increases with time (see Figure 11.4.7). As shown in Figure 11.4.9 b, the resulting voltammogram has a ***peak current*** instead of a limiting current.

For the voltammograms in Figure 11.4.9 a and Figure 11.4.9 b, we measure the current as a function of the applied potential. We also can monitor the change in current, Δi, following a change in potential. The resulting voltammogram, shown in Figure 11.4.9 c, also has a peak current.

QUANTITATIVE AND QUALITATIVE ASPECTS OF VOLTAMMETRY

Earlier we described a voltammogram as the electrochemical equivalent of a spectrum in spectroscopy. In this section we consider how we can extract quantitative and qualitative information from a voltammogram. For simplicity we will limit our treatment to voltammograms similar to Figure 11.4.9 a.

DETERMINING CONCENTRATION

Let's assume that the redox reaction at the working electrode is

$$O + ne^- \rightleftharpoons R \tag{11.4.2}$$

where O is the analyte's oxidized form and R is its reduced form. Let's also assume that only O initially is present in bulk solution and that we are stirring the solution. When we apply a potential that results in the reduction of O to R, the current depends on the rate at which O diffuses through the fixed diffusion layer shown in Figure 11.4.7 . Using Equation 11.4.1, the current, i, is

$$i = K_O\left([O]_{\text{bulk}} - [O]_{x=0}\right) \tag{11.4.3}$$

where K_O is a constant equal to $nFAD_O/\delta$. When we reach the limiting current, i_l, the concentration of O at the electrode surface is zero and Equation 11.4.3 simplifies to

$$i_l = K_O[O]_{\text{bulk}} \tag{11.4.4}$$

Equation 11.4.4 shows us that the limiting current is a linear function of the concentration of O in bulk solution. To determine the value of K_O we can use any of the standardization methods covered in Chapter 5. Equations similar to Equation 11.4.4 can be developed for the other two types of voltammograms shown in Figure 11.4.9 .

DETERMINING THE STANDARD-STATE POTENTIAL

To extract the standard-state potential from a voltammogram, we need to rewrite the Nernst equation for reaction 11.4.2

$$E = E^\circ_{O/R} - \frac{0.05916}{n}\log\frac{[R]_{x=0}}{[O]_{x=0}} \tag{11.4.5}$$

in terms of current instead of the concentrations of O and R. We will do this in several steps. First, we substitute Equation 11.4.4 into Equation 11.4.3 and rearrange to give

$$[O]_{x=0} = \frac{i_l - i}{K_O} \tag{11.4.6}$$

Next, we derive a similar equation for $[R]_{x=0}$, by noting that

$$i = K_R\left([R]_{x=0} - [R]_{\text{bulk}}\right)$$

Because the concentration of $[R]_{\text{bulk}}$ is zero—remember our assumption that the initial solution contains only O—we can simplify this equation

$$i = K_R[R]_{x=0}$$

and solve for $[R]_{x=0}$.

$$[R]_{x=0} = \frac{i}{K_R} \tag{11.4.7}$$

Now we are ready to finish our derivation. Substituting Equation 11.4.7 and Equation 11.4.6 into Equation 11.4.5 and rearranging leaves us with

$$E = E^\circ_{O/R} - \frac{0.05916}{n}\log\frac{K_O}{K_R} - \frac{0.05916}{n}\log\frac{i}{i_l - i} \tag{11.4.8}$$

When the current, i, is half of the limiting current, i_l,

$$i = 0.5 \times i_l$$

we can simplify Equation 11.4.8 to

$$E_{1/2} = E^\circ_{O/R} - \frac{0.05916}{n}\log\frac{K_O}{K_R} \tag{11.4.9}$$

where $E_{1/2}$ is the half-wave potential (Figure 11.4.10). If K_O is approximately equal to K_R, which often is the case, then the half-wave potential is equal to the standard-state potential. Note that Equation 11.4.9 is valid only if the redox reaction is electrochemically reversible.

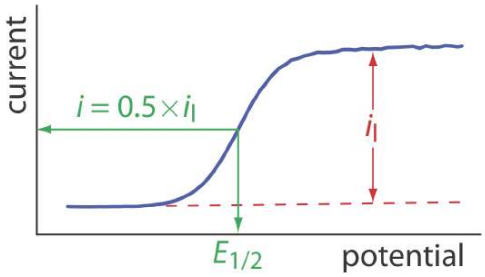


Figure 11.4.10 . Determination of the limiting current, i_l, and the half-wave potential, $E_{1/2}$, for the voltammogram in Figure 11.4.9 a.

VOLTAMMETRIC TECHNIQUES

In voltammetry there are three important experimental parameters under our control: how we change the potential applied to the working electrode, when we choose to measure the current, and whether we choose to stir the solution. Not surprisingly, there are many different voltammetric techniques. In this section we consider several important examples.

POLAROGRAPHY

The first important voltammetric technique to be developed—***polarography***—uses the dropping mercury electrode shown in Figure 11.4.1 b as the working electrode. As shown in Figure 11.4.11 , the current is measured while applying a linear potential ramp.

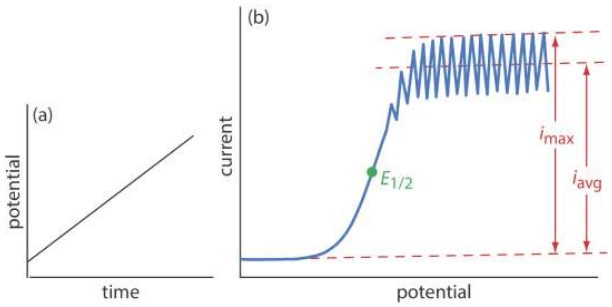


Figure 11.4.11 . Details of normal polarography: (a) the linear potential-excitation signal, and (b) the resulting voltammogram.

Although polarography takes place in an unstirred solution, we obtain a limiting current instead of a peak current. When a Hg drop separates from the glass capillary and falls to the bottom of the electrochemical cell, it mixes the solution. Each new Hg drop, therefore, grows into a solution whose composition is identical to the bulk solution. The oscillations in the current are a result of the Hg drop's growth, which leads to a time-dependent change in the area of the working electrode. The limiting current—which also is called the diffusion current—is measured using either the maximum current, i_{max}, or from the average current, i_{avg}. The relationship between the analyte's concentration, C_A, and the limiting current is given by the Ilkovic equations

$$i_{max} = 706nD^{1/2}m^{2/3}t^{1/6}C_A = K_{max}C_A$$

$$i_{avg} = 607nD^{1/2}m^{2/3}t^{1/6}C_A = K_{avg}C_A$$

where n is the number of electrons in the redox reaction, D is the analyte's diffusion coefficient, m is the flow rate of Hg, t is the drop's lifetime and K_{max} and K_{avg} are constants. The half-wave potential, $E_{1/2}$, provides qualitative information about the redox reaction.

Normal polarography has been replaced by various forms of ***pulse polarography***, several examples of which are shown in Figure 11.4.12 [Osteryoung, J. *J. Chem. Educ.* **1983**, *60*, 296–298]. Normal pulse polarography (Figure 11.4.12 a), for example, uses a series of potential pulses characterized by a cycle of time τ, a pulse-time of t_p, a pulse potential of ΔE_p, and a scan rate of $\Delta E/\Delta t$. Typical experimental conditions for normal pulse polarography are $\tau \approx 1$ s, $t_p \approx 50$ ms, and $\Delta E/\Delta t \approx 2$ mV/s. The initial value of $\Delta E_p \approx 2$ mV, and it increases by ≈ 2 mV with each pulse. The current is sampled at the end of each potential pulse for approximately 17 ms before returning the potential to its initial value. The shape of the resulting voltammogram is similar to Figure 11.4.11 , but without the current oscillations. Because we apply the potential for only a small portion of the drop's lifetime, there is less time for the analyte to undergo oxidation or reduction and a smaller diffusion layer. As a result, the faradaic current in normal pulse polarography is greater than in the polarography, resulting in better sensitivity and smaller detection limits.

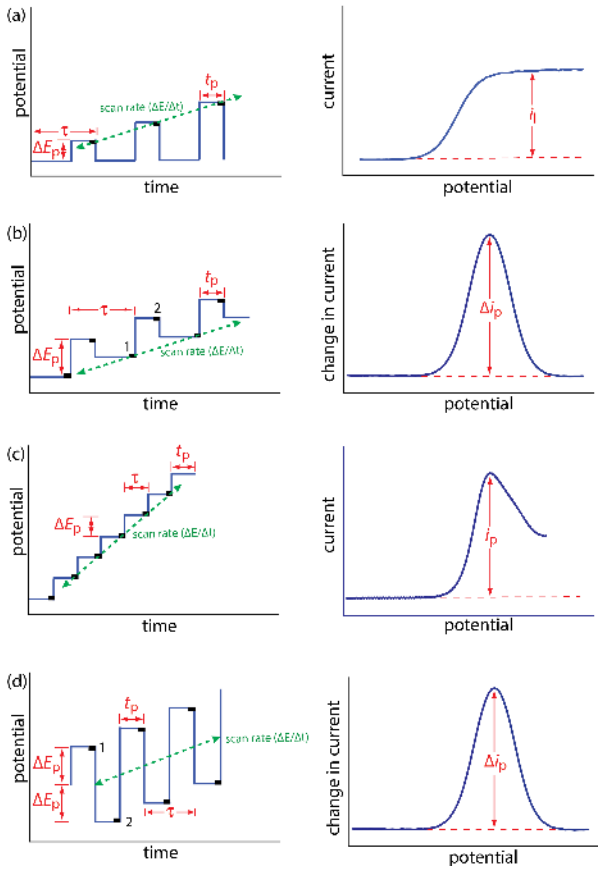


Figure 11.4.12 . Potential-excitation signals and voltammograms for (a) normal pulse polarography, (b) differential pulse polarography, (c) staircase polarography, and (d) square-wave polarography. The current is sampled at the time intervals shown by the black rectangles. When measuring a change in current, Δi, the current at point 1 is subtracted from the current at point 2. The symbols in the diagrams are as follows: τ is the cycle time; ΔE_p is a fixed or variable pulse potential relative to the beginning of the cycle; and t_p is the pulse time. The scan rate (change in potential per unit time) is shown by the dashed arrow.

In differential pulse polarography (Figure 11.4.12 b) the current is measured twice per cycle: for approximately 17 ms before applying the pulse and for approximately 17 ms at the end of the cycle. The difference in the two currents gives rise to the peak-shaped voltammogram. Typical experimental conditions for differential pulse polarography are $\tau \approx 1$ s, $t_p \approx 50$ ms, $\Delta E_p \approx 50$ mV, and $\Delta E/\Delta t \approx 2$ mV/s.

> The voltammogram for differential pulse polarography is approximately the first derivative of the voltammogram for normal pulse polarography. To see why this is the case, note that the change in current over a fixed change in potential, $\Delta i/\Delta E$, approximates the slope of the voltammogram for normal pulse polarography. You may recall that the first derivative of a function returns the slope of the function at each point. The first derivative of a sigmoidal function is a peak-shaped function.

Other forms of pulse polarography include staircase polarography (Figure 11.4.12 c) and square-wave polarography (Figure 11.4.12 d). One advantage of square-wave polarography is that we can make τ very small—perhaps as small as 5 ms, compared to 1 s for other forms of pulse polarography—which significantly decreases analysis time. For example, suppose we need to scan a potential range of 400 mV. If we use normal pulse polarography with a $\Delta E/\Delta t$ of 2 mV/cycle and a τ of 1 s/cycle, then we need 200 s to complete the scan. If we use square-wave polarography with a $\Delta E/\Delta t$ of 2 mV/cycle and a τ of 5 ms/cycle, we can complete the scan in 1 s. At this rate, we can acquire a complete voltammogram using a single drop of Hg!

Polarography is used extensively for the analysis of metal ions and inorganic anions, such as IO_3^- and NO_3^-. We also can use polarography to study organic compounds with easily reducible or oxidizable functional groups, such as carbonyls, carboxylic acids, and carbon-carbon double bonds.

HYDRODYNAMIC VOLTAMMETRY

In polarography we obtain a limiting current because each drop of mercury mixes the solution as it falls to the bottom of the electrochemical cell. If we replace the DME with a solid electrode (see Figure 11.4.3), we can still obtain a limiting current if we mechanically stir the solution during the analysis, using either a stir bar or by rotating the electrode. We call this approach ***hydrodynamic voltammetry***.

Hydrodynamic voltammetry uses the same potential profiles as in polarography, such as a linear scan (Figure 11.4.11) or a differential pulse (Figure 11.4.12 b). The resulting voltammograms are identical to those for polarography, except for the lack of current oscillations from the growth of the mercury drops. Because hydrodynamic voltammetry is not limited to Hg electrodes, it is useful for analytes that undergo oxidation or reduction at more positive potentials.

STRIPPING VOLTAMMETRY

Another important voltammetric technique is ***stripping voltammetry***, which consists of three related techniques: anodic stripping voltammetry, cathodic stripping voltammetry, and adsorptive stripping voltammetry. Because anodic stripping voltammetry is the more widely used of these techniques, we will consider it in greatest detail.

Anodic stripping voltammetry consists of two steps (Figure 11.4.13). The first step is a controlled potential electrolysis in which we hold the working electrode—usually a hanging mercury drop or a mercury film electrode—at a cathodic potential sufficient to deposit the metal ion on the electrode. For example, when analyzing Cu^{2+} the deposition reaction is

$$\mathbf{Cu^{2+} + 2e^- \rightleftharpoons Cu(Hg)}$$

where Cu(Hg) indicates that the copper is amalgamated with the mercury. This step serves as a means of concentrating the analyte by transferring it from the larger volume of the solution to the smaller volume of the electrode. During most of the electrolysis we stir the solution to increase the rate of deposition. Near the end of the deposition time we stop the stirring—eliminating convection as a mode of mass transport—and allow the solution to become quiescent. Typical deposition times of 1–30 min are common, with analytes at lower concentrations requiring longer times.

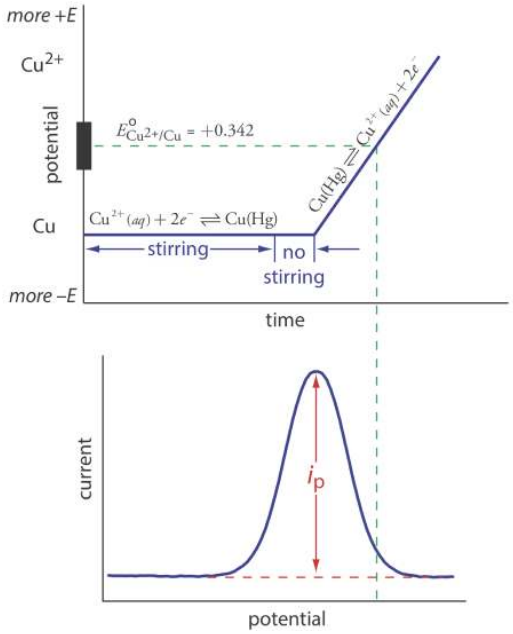


Figure 11.4.13 . Potential-excitation signal and voltammogram for anodic stripping voltammetry at a hanging mercury drop electrode or a mercury film electrode. Note the ladder diagram for copper in the upper figure.

In the second step, we scan the potential anodically—that is, toward a more positive potential. When the working electrode's potential is sufficiently positive, the analyte is stripped from the electrode, returning to solution in its oxidized form.

$$\mathbf{Cu(Hg) \rightleftharpoons\ Cu^{2+} + 2e^-}$$

Monitoring the current during the stripping step gives a peak-shaped voltammogram, as shown in Figure 11.4.13 . The peak current is proportional to the analyte's concentration in the solution. Because we are concentrating the analyte in the electrode, detection limits are much smaller than other electrochemical techniques. An improvement of three orders of magnitude—the equivalent of parts per billion instead of parts per million—is routine.

Anodic stripping voltammetry is very sensitive to experimental conditions, which we must carefully control to obtain results that are accurate and precise. Key variables include the area of the mercury film or the size of the hanging Hg drop, the deposition time, the rest time, the rate of stirring, and the scan rate during the stripping step. Anodic stripping voltammetry is particularly useful for metals that form amalgams with mercury, several examples of which are listed in Table 11.4.1 .

Table 11.4.1 . Representative Examples of Analytes Determined by Stripping Voltammetry

anodic stripping voltammetry	cathodic stripping voltammetry	adsorptive stripping voltammetry
Bi^{3+}	Br^-	bilirubin
Cd^{2+}	Cl^-	codeine
Cu^{2+}	I^-	cocaine
Ga^{3+}	mercaptans (RSH)	digitoxin
In^{3+}	S^{2-}	dopamine
Pb^{2+}	SCN^-	heme
Tl^+		monesin
Sn^{2+}		testosterone
Zn^{2+}		

Source: Compiled from Peterson, W. M.; Wong, R. V. *Am. Lab.* November 1981, 116–128; Wang, J. *Am. Lab.* May 1985, 41–50.

The experimental design for cathodic stripping voltammetry is similar to anodic stripping voltammetry with two exceptions. First, the deposition step involves the oxidation of the Hg electrode to Hg_2^{2+}, which then reacts with the analyte to form an insoluble film at the surface of the electrode. For example, when Cl^- is the analyte the deposition step is

$$2Hg(l) + 2Cl^-(aq) \rightleftharpoons Hg_2Cl_2(s) + 2e^-$$

Second, stripping is accomplished by scanning cathodically toward a more negative potential, reducing Hg_2^{2+} back to Hg and returning the analyte to solution.

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$$

Table 11.4.1 lists several analytes analyzed successfully by cathodic stripping voltammetry.

In adsorptive stripping voltammetry, the deposition step occurs without electrolysis. Instead, the analyte adsorbs to the electrode's surface. During deposition we maintain the electrode at a potential that enhances adsorption. For example, we can adsorb a neutral molecule on a Hg drop if we apply a potential of –0.4 V versus the SCE, a potential where the surface charge of mercury is approximately zero. When deposition is complete, we scan the potential in an anodic or a cathodic direction, depending on whether we are oxidizing or reducing the analyte. Examples of compounds that have been analyzed by absorptive stripping voltammetry also are listed in Table 11.4.1 .

CYCLIC VOLTAMMETRY

In the voltammetric techniques consider to this point we scan the potential in one direction, either to more positive potentials or to more negative potentials. In ***cyclic voltammetry*** we complete a scan in both directions. Figure 11.4.14 a shows a typical potential-excitation signal. In this example, we first scan the potential to more positive values, resulting in the following oxidation reaction for the species *R*.

$$R \rightleftharpoons O + ne^-$$

When the potential reaches a predetermined switching potential, we reverse the direction of the scan toward more negative potentials. Because we generated the species *O* on the forward scan, during the reverse scan it reduces back to *R*.

$$O + ne^- \rightleftharpoons R$$

Cyclic voltammetry is carried out in an unstirred solution, which, as shown in Figure 11.4.14 b, results in peak currents instead of limiting currents. The voltammogram has separate peaks for the oxidation reaction and for the reduction reaction, each characterized by a peak potential and a peak current.

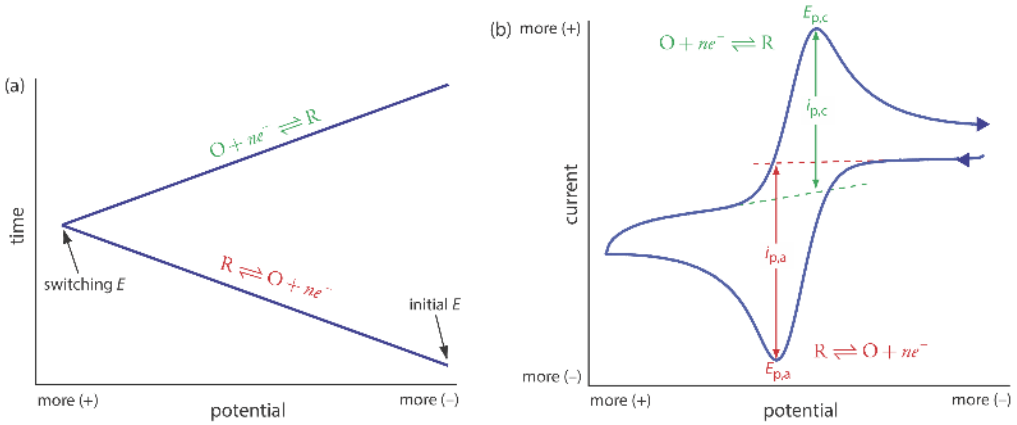


Figure 11.4.14 . Details for cyclic voltammetry. (a) One cycle of the triangular potential-excitation signal showing the initial potential and the switching potential. A cyclic voltammetry experiment can consist of one cycle or many cycles. Although the initial potential in this example is the negative switching potential, the cycle can begin with an intermediate initial potential and cycle between two limits. (b) The resulting cyclic voltammogram showing the measurement of the peak currents and peak potentials.

The peak current in cyclic voltammetry is given by the Randles-Sevcik equation

$$i_p = \left(2.69 \times 10^5\right) n^{3/2} A D^{1/2} \nu^{1/2} C_A$$

where n is the number of electrons in the redox reaction, A is the area of the working electrode, D is the diffusion coefficient for the electroactive species, ν is the scan rate, and C_A is the concentration of the electroactive species at the electrode. For a well-behaved system, the anodic and the cathodic peak currents are equal, and the ratio $i_{p,a}/i_{p,c}$ is 1.00. The half-wave potential, $E_{1/2}$, is midway between the anodic and cathodic peak potentials.

$$E_{1/2} = \frac{E_{p,a} + E_{p,c}}{2}$$

Scanning the potential in both directions provides an opportunity to explore the electrochemical behavior of species generated at the electrode. This is a distinct advantage of cyclic voltammetry over other voltammetric techniques. Figure 11.4.15 shows the cyclic voltammogram for the same redox couple at both a faster and a slower scan rate. At the faster scan rate, 11.4.15 a, we see two peaks. At the slower scan rate in Figure 11.4.15 b, however, the peak on the reverse scan disappears. One explanation for this is that the products from the reduction of R on the forward scan have sufficient time to participate in a chemical reaction whose products are not electroactive.

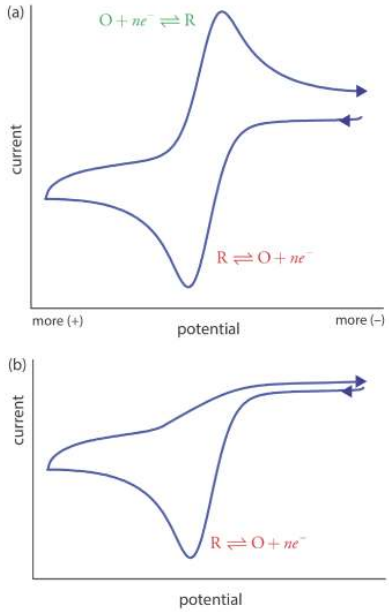


Figure 11.4.15 . Cyclic voltammograms for R obtained at (a) a faster scan rate and at (b) a slower scan rate. One of the principal uses of cyclic voltammetry is to study the chemical and electrochemical behavior of compounds. See this chapter's additional resources for further information.

AMPEROMETRY

The final voltammetric technique we will consider is ***amperometry***, in which we apply a constant potential to the working electrode and measure current as a function of time. Because we do not vary the potential, amperometry does not result in a voltammogram.

One important application of amperometry is in the construction of chemical sensors. One of the first amperometric sensors was developed in 1956 by L. C. Clark to measure dissolved O_2 in blood. Figure 11.4.16 shows the sensor's design, which is similar to a potentiometric membrane electrode. A thin, gas-permeable membrane is stretched across the end of the sensor and is separated from the working electrode and the counter electrode by a thin solution of KCl. The working electrode is a Pt disk cathode, and a Ag ring anode serves as the counter electrode. Although several gases can diffuse across the membrane, including O_2, N_2, and CO_2, only oxygen undergoes reduction at the cathode

$$\mathrm{O_2}(g) + 4\mathrm{H_3O^+}(aq) + 4e^- \rightleftharpoons 6\mathrm{H_2O}(l)$$

with its concentration at the electrode's surface quickly reaching zero. The concentration of O_2 at the membrane's inner surface is fixed by its diffusion through the membrane, which creates a diffusion profile similar to that in Figure 11.4.8 . The result is a steady-state current that is proportional to the concentration of dissolved oxygen. Because the electrode consumes oxygen,the sample is stirred to prevent the depletion of O_2 at the membrane's outer surface.

> The oxidation of the Ag anode is the other half-reaction.
>
> $$\mathrm{Ag}(s) + \mathrm{Cl^-}(aq) \rightleftharpoons \mathrm{AgCl}(s) + e^-$$

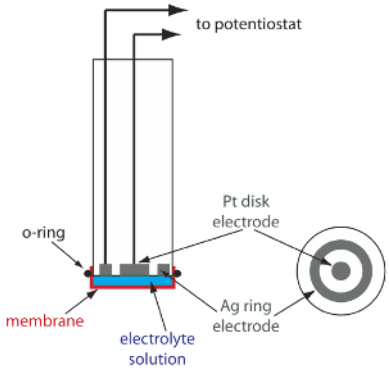


Figure 11.4.16 . Clark amperometric sensor for determining dissolved O_2. The diagram on the right is a cross-section through the electrode, which shows the Ag ring electrode and the Pt disk electrode.

Another example of an amperometric sensor is a glucose sensor. In this sensor the single membrane in Figure 11.4.16 is replaced with three membranes. The outermost membrane of polycarbonate is permeable to glucose and O_2. The second membrane contains an immobilized preparation of glucose oxidase that catalyzes the oxidation of glucose to gluconolactone and hydrogen peroxide.

$$\beta - \mathrm{D{-}glucose}\ (aq) + \mathrm{O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{gluconolactone}\ (aq) + \mathrm{H_2O_2}(aq)$$

The hydrogen peroxide diffuses through the innermost membrane of cellulose acetate where it undergoes oxidation at a Pt anode.

$$\mathrm{H_2O_2}(aq) + 2\mathrm{OH^-}(aq) \rightleftharpoons \mathrm{O_2}(aq) + 2\mathrm{H_2O}(l) + 2e^-$$

Figure 11.4.17 summarizes the reactions that take place in this amperometric sensor. FAD is the oxidized form of flavin adenine nucleotide —the active site of the enzyme glucose oxidase—and $FADH_2$ is the active site's reduced form. Note that O_2 serves a mediator, carrying electrons to the electrode.

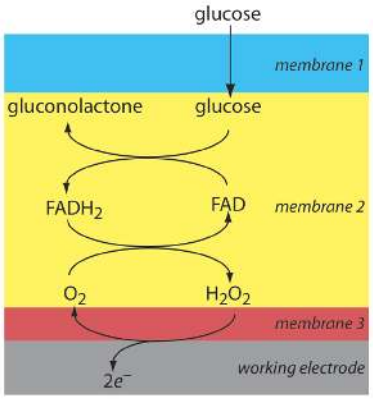


Figure 11.4.17 . Schematic showing the reactions by which an amperometric biosensor responds to glucose.

By changing the enzyme and mediator, it is easy to extend to the amperometric sensor in Figure 11.4.17 to the analysis of other analytes. For example, a CO_2 sensor has been developed using an amperometric O_2 sensor with a two-layer membrane, one of which contains an immobilized preparation of autotrophic bacteria [Karube, I.; Nomura, Y.; Arikawa, Y. *Trends in Anal. Chem.* **1995**, *14*, 295–299]. As CO_2 diffuses through the membranes it is converted to O_2 by the bacteria, increasing the concentration of O_2 at the Pt cathode.

QUANTITATIVE APPLICATIONS

Voltammetry has been used for the quantitative analysis of a wide variety of samples, including environmental samples, clinical samples, pharmaceutical formulations, steels, gasoline, and oil.

SELECTING THE VOLTAMMETRIC TECHNIQUE

The choice of which voltammetric technique to use depends on the sample's characteristics, including the analyte's expected concentration and the sample's location. For example, amperometry is ideally suited for detecting analytes in flow systems, including the *in vivo* analysis of a patient's blood or as a selective sensor for the rapid analysis of a single analyte. The portability of amperometric sensors, which are similar to potentiometric sensors, also make them ideal for field studies. Although cyclic voltammetry is used to determine an analyte's concentration, other methods described in this chapter are better suited for quantitative work.

Pulse polarography and stripping voltammetry frequently are interchangeable. The choice of which technique to use often depends on the analyte's concentration and the desired accuracy and precision. Detection limits for normal pulse polarography generally are on the order of 10^{-6} M to 10^{-7} M, and those for differential pulse polarography, staircase, and square wave polarography are between 10^{-7} M and 10^{-9} M. Because we concentrate the analyte in stripping voltammetry, the detection limit for many analytes is as little as 10^{-10} M to 10^{-12} M. On the other hand, the current in stripping voltammetry is much more sensitive than pulse polarography to changes in experimental conditions, which may lead to poorer precision and accuracy. We also can use pulse polarography to analyze a wider range of inorganic and organic analytes because there is no need to first deposit the analyte at the electrode surface.

Stripping voltammetry also suffers from occasional interferences when two metals, such as Cu and Zn, combine to form an intermetallic compound in the mercury amalgam. The deposition potential for Zn . is sufficiently negative that any Cu^{2+} in the sample also deposits into the mercury drop or film, leading to the formation of intermetallic compounds such as CuZn and $CuZn_2$. During the stripping step, zinc in the intermetallic compounds strips at potentials near that of copper, decreasing the current for zinc at its usual potential and increasing the apparent current for copper. It is possible to overcome this problem by adding an element that forms a stronger intermetallic compound with the interfering metal. Thus, adding Ga^{3+} minimizes the interference of Cu when analyzing for Zn by forming an intermetallic compound of Cu and Ga.

CORRECTING THE RESIDUAL CURRENT

In any quantitative analysis we must correct the analyte's signal for signals that arise from other sources. The total current, i_{tot}, in voltammetry consists of two parts: the current from the analyte's oxidation or reduction, i_A, and a background or residual current, i_r.

$$i_{tot} = i_A + i_r$$

The residual current, in turn, has two sources. One source is a faradaic current from the oxidation or reduction of trace interferents in the sample, i_{int}. The other source is the charging current, i_{ch}, that accompanies a change in the working electrode's potential.

$$i_r = i_{int} + i_{ch}$$

We can minimize the faradaic current due to impurities by carefully preparing the sample. For example, one important impurity is dissolved O_2, which undergoes a two-step reduction: first to H_2O_2 at a potential of –0.1 V versus the SCE, and then to H_2O at a potential of –0.9 V versus the SCE. Removing dissolved O_2 by bubbling an inert gas such as N_2 through the sample eliminates this interference. After removing the dissolved O_2, maintaining a blanket of N_2 over the top of the solution prevents O_2 from reentering the solution.

> The cell in Figure 11.4.4 shows a typical N_2 purge line.

There are two methods to compensate for the residual current. One method is to measure the total current at potentials where the analyte's faradaic current is zero and extrapolate it to other potentials. This is the method shown in Figure 11.4.9 . One advantage of extrapolating is that we do not need to acquire additional data. An important disadvantage is that an extrapolation assumes that any change in the residual current with potential is predictable, which may not be the case. A second, and more rigorous approach, is to obtain a voltammogram for an appropriate blank. The blank's residual current is then subtracted from the sample's total current.

ANALYSIS FOR SINGLE COMPONENTS

The analysis of a sample with a single analyte is straightforward using any of the standardization methods discussed in Chapter 5.

✔ EXAMPLE 11.4.1

The concentration of As(III) in water is determined by differential pulse polarography in 1 M HCl. The initial potential is set to –0.1 V versus the SCE and is scanned toward more negative potentials at a rate of 5 mV/s. Reduction of As(III) to As(0) occurs at a potential of approximately –0.44 V versus the SCE. The peak currents for a set of standard solutions, corrected for the residual current, are shown in the following table.

[As(III)] (μM)	i_p (μM)
1.00	0.298
3.00	0.947
6.00	1.83
9.00	2.72

What is the concentration of As(III) in a sample of water if its peak current is 1.37 μA?

Solution

Linear regression gives the calibration curve shown in Figure 11.4.18 , with an equation of

$$i_p = 0.0176 + 3.01 \times [\text{As(III)}]$$

Substituting the sample's peak current into the regression equation gives the concentration of As(III) as 4.49 μM.

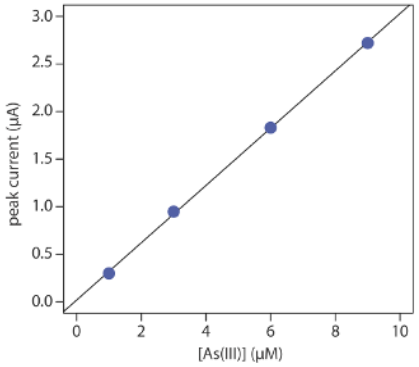


Figure 11.4.18 . Calibration curve for the data in Example 11.4.1 .

? EXERCISE 11.4.1

The concentration of copper in a sample of sea water is determined by anodic stripping voltammetry using the method of standard additions. The analysis of a 50.0-mL sample gives a peak current of 0.886 μA. After adding a 5.00-μL spike of 10.0 mg/L Cu^{2+}, the peak current increases to 2.52 μA. Calculate the μg/L copper in the sample of sea water.

Answer

For anodic stripping voltammetry, the peak current, i_p, is a linear function of the analyte's concentration

$$i_p = K \times C_{Cu}$$

where K is a constant that accounts for experimental parameters such as the electrode's area, the diffusion coefficient for Cu^{2+}, the deposition time, and the rate of stirring. For the analysis of the sample before the standard addition we know that the current is

$$i_p = 0.886\ \mu A = K \times C_{Cu}$$

and after the standard addition the current is

$$i_p = 2.52\ \mu A = K\left\{C_{Cu} \times \frac{50.00\ mL}{50.005\ mL} + \frac{10.00 mg Cu}{L} \times \frac{0.005\ mL}{50.005\ mL}\right\}$$

where 50.005 mL is the total volume after we add the 5.00 µL spike. Solving each equation for K and combining leaves us with the following equation.

$$\frac{0.886\ \mu A}{C_{Cu}} = K = \frac{2.52\ \mu A}{C_{Cu} \times \frac{50.00\ mL}{50.005\ mL} + \frac{10.00\ mg\ Cu}{L} \times \frac{0.005\ mL}{50.005\ mL}}$$

Solving this equation for C_{Cu} gives its value as 5.42×10^{-4} mg Cu^{2+}/L, or 0.542 µg Cu^{2+}/L.

MULTICOMPONENT ANALYSIS

Voltammetry is a particularly attractive technique for the analysis of samples that contain two or more analytes. Provided that the analytes behave independently, the voltammogram of a multicomponent mixture is a summation of each analyte's individual voltammograms. As shown in Figure 11.4.19 , if the separation between the half-wave potentials or between the peak potentials is sufficient, we can determine the presence of each analyte as if it is the only analyte in the sample. The minimum separation between the half-wave potentials or peak potentials for two analytes depends on several factors, including the type of electrode and the potential-excitation signal. For normal polarography the separation is at least ±0.2–0.3 V, and differential pulse voltammetry requires a minimum separation of ±0.04–0.05 V.

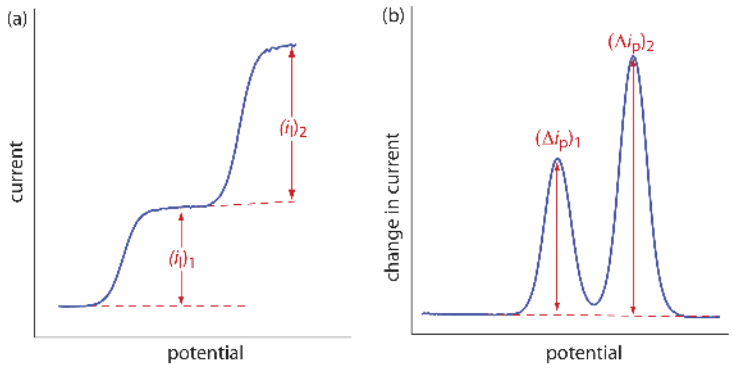


Figure 11.4.19 . Voltammograms for a sample that contains two analytes showing the measurement of (a) limiting currents, and (b) peak currents.

If the voltammograms for two analytes are not sufficiently separated, a simultaneous analysis may be possible. An example of this approach is outlined the following example.

✔ EXAMPLE 11.4.2

The differential pulse polarographic analysis of a mixture of indium and cadmium in 0.1 M HCl is complicated by the overlap of their respective voltammograms [Lanza P. *J. Chem. Educ.* **1990**, *67*, 704–705]. The peak potential for indium is at –0.557 V and that for cadmium is at –0.597 V. When a 0.800-ppm indium standard is analyzed, Δi_p (in arbitrary units) is 200.5 at –0.557 V and 87.5 at –0.597 V relative to a saturated Ag/AgCl reference electorde. A standard solution of 0.793 ppm cadmium has a Δi_p of 58.5 at –0.557 V and 128.5 at –0.597 V. What is the concentration of indium and cadmium in a sample if Δi_p is 167.0 at a potential of –0.557 V and 99.5 at a potential of –0.597V.

Solution

The change in current, Δi_p, in differential pulse polarography is a linear function of the analyte's concentration

$$\Delta i_p = k_A C_A$$

where k_A is a constant that depends on the analyte and the applied potential, and C_A is the analyte's concentration. To determine the concentrations of indium and cadmium in the sample we must first find the value of k_A for each analyte at each potential. For simplicity we will identify the potential of –0.557 V as E_1, and that for –0.597 V as E_2. The values of k_A are

$$k_{\text{In},E_1} = \frac{200.5}{0.800 \text{ ppm}} = 250.6 \text{ ppm}^{-1}$$
$$k_{\text{In},E_2} = \frac{87.5}{0.800 \text{ ppm}} = 109.4 \text{ ppm}^{-1}$$
$$k_{\text{Cd}E_1} = \frac{58.5}{0.793 \text{ ppm}} = 73.8 \text{ ppm}^{-1}$$
$$k_{\text{Cd}E_2} = \frac{128.5}{0.793 \text{ ppm}} = 162.0 \text{ ppm}^{-1}$$

Next, we write simultaneous equations for the current at the two potentials.

$$\Delta i_{E_1} = 167.0 = 250.6 \text{ ppm}^{-1} \times C_{\text{In}} + 73.8 \text{ ppm}^{-1} \times C_{\text{Cd}}$$
$$\Delta i_{E_2} = 99.5 = 109.4 \text{ ppm}^{-1} \times C_{\text{In}} + 162.0 \text{ ppm}^{-1} \times C_{\text{Cd}}$$

Solving the simultaneous equations, which is left as an exercise, gives the concentration of indium as 0.606 ppm and the concentration of cadmium as 0.205 ppm.

ENVIRONMENTAL SAMPLES

Voltammetry is one of several important analytical techniques for the analysis of trace metals in environmental samples, including groundwater, lakes, rivers and streams, seawater, rain, and snow. Detection limits at the parts-per-billion level are routine for many trace metals using differential pulse polarography, with anodic stripping voltammetry providing parts-per-trillion detection limits for some trace metals.

One interesting environmental application of anodic stripping voltammetry is the determination of a trace metal's chemical form within a water sample. Speciation is important because a trace metal's bioavailability, toxicity, and ease of transport through the environment often depends on its chemical form. For example, a trace metal that is strongly bound to colloidal particles generally is not toxic because it is not available to aquatic lifeforms. Unfortunately, anodic stripping voltammetry can not distinguish a trace metal's exact chemical form because closely related species, such as Pb^{2+} and $PbCl^{+}$, produce a single stripping peak. Instead, trace metals are divided into "operationally defined" categories that have environmental significance.

Operationally defined means that an analyte is divided into categories by the specific methods used to isolate it from the sample. There are many examples of operational definitions in the environmental literature. The distribution of trace metals in soils and sediments, for example, often is defined in terms of the reagents used to extract them; thus, you might find an operational definition for Zn^{2+} in a lake sediment as that extracted using 1.0 M sodium acetate, or that extracted using 1.0 M HCl.

Although there are many speciation schemes in the environmental literature, we will consider one proposed by Batley and Florence [see (a) Batley, G. E.; Florence, T. M. *Anal. Lett.* **1976**, *9*, 379–388; (b) Batley, G. E.; Florence, T. M. *Talanta* **1977**, *24*, 151–158; (c) Batley, G. E.; Florence, T. M. *Anal. Chem.* **1980**, *52*, 1962–1963; (d) Florence, T. M., Batley, G. E.; *CRC Crit. Rev. Anal. Chem.* **1980**, *9*, 219–296]. This scheme, which is outlined in Table 11.4.2 , combines anodic stripping voltammetry with ion-exchange and UV irradiation, dividing soluble trace metals into seven groups. In the first step, anodic stripping voltammetry in a pH 4.8 acetic acid buffer differentiates between labile metals and nonlabile metals. Only labile metals—those present as hydrated ions, weakly bound complexes, or weakly adsorbed on colloidal surfaces—deposit at the electrode and give rise to a signal. Total metal concentration are determined by ASV after digesting the sample in 2 M HNO_3 for 5 min, which converts all metals into an ASV-labile form.

Table 11.4.2 . Operational Speciation of Soluble Trace Metals

method	speciation of soluble metals						
ASV	labile metals			nonlabile or bound metals			
Ion-Exchange	removed	not removed		removed		not removed	
UV Irradiation		released	not released	released	not released	released	not released
Groups	I	II	III	IV	V	VI	VII
Group I: free metal ions; weaker labile organic complexes and inorganic complexes							
Group II: stronger labile organic complexes; labile metals absorbed on organic solids							
Group III: stronger labile inorganic complexes; labile metals absorbed on inorganic solids							
Group IV: weaker nonlabile organic complexes							
Group V: weaker nonlabile inorganic complexes							
Group VI: stronger nonlabile organic complexes; nonlabile metals absorbed on organic solids							
Group VII: stronger nonlabile inorganic complexes; nonlabile metals absorbed on inorganic solids							
Operational definitions of speciation from (a)Batley,G.E.;Florence,T.M.*Anal.Lett.***1976**,*9*,379–388;(b)Batley,G.E.;Florence,T.M.*Talanta***1977**,*24*,151–158; (c) Batley, G. E.; Florence, T. M. *Anal. Chem.* **1980**, *52*, 1962–1963; (d) Florence, T. M., Batley, G. E.; *CRC Crit. Rev. Anal. Chem.* **1980**, *9*, 219–296.							

A Chelex-100 ion-exchange resin further differentiates between strongly bound metals—usually metals bound to inorganic and organic solids, but also those tightly bound to chelating ligands—and more loosely bound metals. Finally, UV radiation differentiates between metals bound to organic phases and inorganic phases. The analysis of seawater samples, for example, suggests that cadmium, copper, and lead are present primarily as labile organic complexes or as labile adsorbates on organic colloids (Group II in Table 11.4.2).

Differential pulse polarography and stripping voltammetry are used to determine trace metals in airborne particulates, incinerator fly ash, rocks, minerals, and sediments. The trace metals, of course, are first brought into solution using a digestion or an extraction.

Amperometric sensors also are used to analyze environmental samples. For example, the dissolved O_2 sensor described earlier is used to determine the level of dissolved oxygen and the biochemical oxygen demand, or BOD, of waters and wastewaters. The latter test—which is a measure of the amount of oxygen required by aquatic bacteria as they decompose organic matter—is important when evaluating the efficiency of a wastewater treatment plant and for monitoring organic pollution in natural waters. A high BOD suggests that the water has a high concentration of organic matter. Decomposition of this organic matter may seriously deplete the level of dissolved oxygen in the water, adversely affecting aquatic life. Other amperometric sensors are available to monitor anionic surfactants in water, and CO_2, H_2SO_4, and NH_3 in atmospheric gases.

CLINICAL SAMPLES

Differential pulse polarography and stripping voltammetry are used to determine the concentration of trace metals in a variety of clinical samples, including blood, urine, and tissue. The determination of lead in blood is of considerable interest due to concerns about lead poisoning. Because the concentration of lead in blood is so small, anodic stripping voltammetry frequently is the more appropriate technique. The analysis is complicated, however, by the presence of proteins that may adsorb to the mercury electrode, inhibiting either the deposition or stripping of lead. In addition, proteins may prevent the electrodeposition of lead through the formation of stable, nonlabile complexes. Digesting and ashing the blood sample mini- mizes this problem. Differential pulse polarography is useful for the routine quantitative analysis of drugs in biological fluids, at concentrations of less than 10^{-6} M [Brooks, M. A. “Application of Electrochemistry to Pharmaceutical Analysis,” Chapter 21 in Kissinger, P. T.; Heinemann, W. R., eds. *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker, Inc.: New York, 1984, pp 539–568.]. Amperometric sensors using enzyme catalysts also have many clinical uses, several examples of which are shown in Table 11.4.3 .

Table 11.4.3 . Representative Amperometric Biosensors

analyte	enzyme	species detected
choline	choline oxidase	H_2O_2
ethanol	alcohol oxidase	H_2O_2
formaldehyde	formaldehyde dehydrogenase	NADH
glucose	glucose oxidase	H_2O_2
glutamine	glutaminase, glutamine oxidase	H_2O_2
glycerol	glycerol dehydrogenase	NADH, O_2
lactate	lactate oxidase	H_2O_2
phenol	polyphenol oxidase	quinone
inorganic phosphorous	nucleoside phosphoylase	O_2

Source: Cammann, K.; Lemke, U.; Rohen, A.; Sander, J.; Wilken, H.; Winter, B. *Angew. Chem. Int. Ed. Engl*. **1991**, *30*, 516–539.

MISCELLANEOUS SAMPLES

In addition to environmental samples and clinical samples, differential pulse polarography and stripping voltammetry are used for the analysis of trace metals in other sample, including food, steels and other alloys, gasoline, gunpowder residues, and pharmaceuticals. Voltammetry is an important technique for the quantitative analysis of organics, particularly in the pharmaceutical industry where it is used to determine the concentration of drugs and vitamins in formulations. For example, voltammetric methods are available for the quantitative analysis of vitamin A, niacinamide, and riboflavin. When the compound of interest is not electroactive, it often can be derivatized to an electroactive form. One example is the differential pulse polarographic determination of sulfanilamide, which is converted into an electroactive azo dye by coupling with sulfamic acid and 1-napthol.

REPRESENTATIVE METHOD 11.4.1: DETERMINATION OF CHLOROPROMAZINE IN A PHARMACEUTICAL PRODUCT

The best way to appreciate the theoretical and the practical details discussed in this section is to carefully examine a typical analytical method. Although each method is unique, the following description of the determination of chloropromazine in a pharmaceutical product provides an instructive example of a typical procedure. The description here is based on a method from Pungor, E. *A Practical Guide to Instrumental Analysis*, CRC Press: Boca Raton, FL, 1995, pp. 34–37.

Description of Method

Chlorpromazine, also is known by its trade name Thorazine, is an antipsychotic drug used in the treatment of schizophrenia. The amount of chlorpromazine in a pharmaceutical product is determined voltammetrically at a graphite working electrode in a unstirred solution, with calibration by the method of standard additions.

Procedure

Add 10.00 mL of an electrolyte solution consisting of 0.01 M HCl and 0.1 M KCl to the electrochemical cell. Place a graphite working electrode, a Pt auxiliary electrode, and a SCE reference electrode in the cell, and record the voltammogram from 0.2 V to 2.0 V at a scan rate of 50 mV/s. Weigh out an appropriate amount of the pharmaceutical product and dissolve it in a small amount of the electrolyte. Transfer the solution to a 100-mL volumetric flask and dilute to volume with the electrolyte. Filter a small amount of the diluted solution and transfer 1.00 mL of the filtrate to the voltammetric cell. Mix the contents of the voltammetric cell and allow the solution to sit for 10 s before recording the voltammogram. Return the potential to 0.2 V, add 1.00 mL of a chlorpromazine standard and record the voltammogram. Report the %w/w chlorpromazine in the formulation.

Questions

1. Is chlorpromazine undergoing oxidation or reduction at the graphite working electrode?

Because we are scanning toward more positive potentials, we are oxidizing chlorpromazine.

2. Why does this procedure use a graphite electrode instead of a Hg electrode?

As shown in Figure 11.4.2 , the potential window for a Hg electrode extends from approximately –0.3 V to between –1V and –2 V, depending on the pH. Because we are scanning the potential from 0.2 V to 2.0 V, we cannot use a Hg electrode.

3. Many voltammetric procedures require that we first remove dissolved O_2 by bubbling N_2 through the solution. Why is this not necessary for this analysis?

Dissolved O_2 is a problem when we scan toward more negative potentials, because its reduction may produce a significant cathodic current. In this procedure we are scanning toward more positive potentials and generating anodic currents; thus, dissolved O_2 is not an interferent and does not need to be removed.

4. What is the purpose of recording a voltammogram in the absence of chlorpromazine?

This voltammogram serves as a blank, which provides a measurement of the residual current due to the electrolyte. Because the potential window for a graphite working electrode (see Figure 11.4.2) does not extend to 2.0 V, there is a measurable anodic residual current due to the solvent's oxidation. Having measured this residual current, we can subtract it from the total current in the presence of chlorpromazine.

5. Based on the description of this procedure, what is the shape of the resulting voltammogram. You may wish to review the three common shapes shown in Figure 11.4.9 .

Because the solution is unstirred, the voltammogram will have a peak current similar to that shown in Figure 11.4.9 b.

CHARACTERIZATION APPLICATIONS

In the previous section we learned how to use voltammetry to determine an analyte's concentration in a variety of different samples. We also can use voltammetry to characterize an analyte's properties, including verifying its electrochemical reversibility, determining the number of electrons transferred during its oxidation or reduction, and determining its equilibrium constant in a coupled chemical reaction.

ELECTROCHEMICAL REVERSIBILITY AND DETERMINATION OF *N*

Earlier in this chapter we derived a relationship between $E_{1/2}$ and the standard-state potential for a redox couple (Equation 11.4.9), noting that a redox reaction must be electrochemically reversible. How can we tell if a redox reaction is reversible by looking at its voltammogram? For a reversible redox reaction Equation 11.4.8, which we repeat here, describes the relationship between potential and current for a voltammetric experiment with a limiting current.

$$E = E^\circ_{O/R} - \frac{0.05916}{n}\log\frac{K_O}{K_R} - \frac{0.05916}{n}\log\frac{i}{i_l - i}$$

If a reaction is electrochemically reversible, a plot of E versus $\log(i/i_l - i)$ is a straight line with a slope of $-0.05916/n$. In addition, the slope should yield an integer value for n.

EXAMPLE 11.4.3

The following data were obtained from a linear scan hydrodynamic voltammogram of a reversible reduction reaction.

E (V vs. SCE)	current (μA)
–0.358	0.37
–0.372	0.95
–0.382	1.71
–0.400	3.48
–0.410	4.20
–0.435	4.97

The limiting current is 5.15 μA. Show that the reduction reaction is reversible, and determine values for n and for $E_{1/2}$.

Solution

Figure 11.4.20 shows a plot of E versus $\log(i/i_l - i)$. Because the result is a straight-line, we know the reaction is electrochemically reversible under the conditions of the experiment. A linear regression analysis gives the equation for the straight line as

$$E = -0.391\text{V} - 0.0300\log\frac{i}{i_l - i}$$

From Equation 11.4.8, the slope is equivalent to $-0.05916/n$; solving for n gives a value of 1.97, or 2 electrons. From Equation 11.4.8 and Equation 11.4.9, we know that $E_{1/2}$ is the y-intercept for a plot of E versus $\log(i/i_l - i)$; thus, $E_{1/2}$ for the data in this example is –0.391 V versus the SCE.

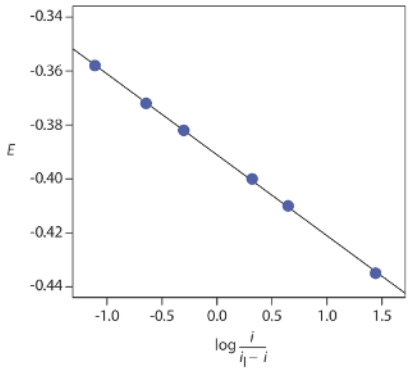


Figure 11.4.20 . Determination of electrochemical reversibility for the data in Example 11.4.3 .

We also can use cyclic voltammetry to evaluate electrochemical reversibility by looking at the difference between the peak potentials for the anodic and the cathodic scans. For an electrochemically reversible reaction, the following equation holds true.

$$\Delta E_p = E_{p,a} - E_{p,c} = \frac{0.05916 \text{ V}}{n}$$

As an example, for a two-electron reduction we expect a ΔE_p of approximately 29.6 mV. For an electrochemically irreversible reaction the value of ΔE_p is larger than expected.

DETERMINING EQUILIBRIUM CONSTANTS FOR COUPLED CHEMICAL REACTIONS

Another important application of voltammetry is determining the equilibrium constant for a solution reaction that is coupled to a redox reaction. The presence of the solution reaction affects the ease of electron transfer in the redox reaction, shifting $E_{1/2}$ to a more negative or to a more positive potential. Consider, for example, the reduction of O to R

$$O + ne^- \rightleftharpoons R$$

the voltammogram for which is shown in Figure 11.4.21 . If we introduce a ligand, L, that forms a strong complex with O, then we also must consider the reaction

$$O + pL \rightleftharpoons OL_p$$

In the presence of the ligand, the overall redox reaction is

$$OL_p + ne^- \rightleftharpoons R + pL$$

Because of its stability, the reduction of the OL_p complex is less favorable than the reduction of O. As shown in Figure 11.4.21 , the resulting voltammogram shifts to a potential that is more negative than that for O. Furthermore, the shift in the voltammogram increases as we increase the ligand's concentration.

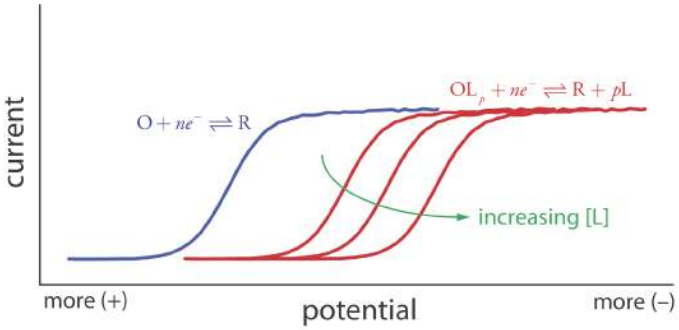


Figure 11.4.21 . Effect of a metal-ligand complexation reaction on a voltammogram. The voltammogram in blue is for the reduction of O in the absence of ligand. Adding the ligand shifts the potentials to more negative potentials, as shown by the voltammograms in red.

We can use this shift in the value of $E_{1/2}$ to determine both the stoichiometry and the formation constant for a metal-ligand complex. To derive a relationship between the relevant variables we begin with two equations: the Nernst equation for the reduction of O

$$E = E^\circ_{O/R} - \frac{0.05916}{n} \log \frac{[R]_{x=0}}{[O]_{x=0}} \tag{11.4.10}$$

and the stability constant, β_p for the metal-ligand complex at the electrode surface.

$$\beta_p = \frac{[OL_p]_{x=0}}{[O]_{x=0}[L]^p_{x=0}} \tag{11.4.11}$$

In the absence of ligand the half-wave potential occurs when $[R]_{x\,=\,0}$ and $[O]_{x\,=\,0}$ are equal; thus, from the Nernst equation we have

$$(E_{1/2})_{nc} = E^\circ_{O/R} \tag{11.4.12}$$

where the subscript "*nc*" signifies that the complex is not present.

When ligand is present we must account for its effect on the concentration of *O*. Solving Equation 11.4.1 for $[O]_{x\,=\,0}$ and substituting into the Equation 11.4.10 gives

$$E = E^\circ_{O/R} - \frac{0.05916}{n}\log\frac{[R]_{x=0}[L]^p_{x=0}\beta_p}{[OL_p]_{x=0}} \tag{11.4.13}$$

If the formation constant is sufficiently large, such that essentially all *O* is present as the complex OL_p, then $[R]_{x\,=\,0}$ and $[OL_p]_{x\,=\,0}$ are equal at the half-wave potential, and Equation 11.4.13 simplifies to

$$(E_{1/2})_c = E^\circ_{O/R} - \frac{0.05916}{n}\log[L]^p_{x=0}\beta_p \tag{11.4.14}$$

where the subscript "*c*" indicates that the complex is present. Defining $\Delta E_{1/2}$ as

$$\triangle E_{1/2} = (E_{1/2})_c - (E_{1/2})_{nc} \tag{11.4.15}$$

and substituting Equation 11.4.12 and Equation 11.4.14 and expanding the log term leaves us with the following equation.

$$\Delta E_{1/2} = -\frac{0.05916}{n}\log\beta_p - \frac{0.05916p}{n}\log[L] \tag{11.4.16}$$

A plot of $\Delta E_{1/2}$ versus log[*L*] is a straight-line, with a slope that is a function of the metal-ligand complex's stoichiometric coefficient, *p*, and a *y*-intercept that is a function of its formation constant β_p.

EXAMPLE 11.4.4

A voltammogram for the two-electron reduction (n = 2) of a metal, *M*, has a half-wave potential of –0.226 V versus the SCE. In the presence of an excess of ligand, *L*, the following half-wave potentials are recorded.

[*L*] (M)	$(E_{1/2})_c$ (V vs. SCE)
0.020	–0.494
0.040	–0.512
0.060	–0.523
0.080	–0.530
0.100	–0.536

Determine the stoichiometry of the metal-ligand complex and its formation constant.

Solution

We begin by calculating values of $\Delta E_{1/2}$ using Equation 11.4.15, obtaining the values in the following table.

[*L*] (M)	$\Delta E_{1/2}$ (V vs. SCE)
0.020	–0.268
0.040	–0.286
0.060	–0.297
0.080	–0.304
0.100	–0.310

Figure 11.4.22 shows the resulting plot of $\Delta E_{1/2}$ as a function of log[*L*]. A linear regression analysis gives the equation for the straight line as

$$\triangle E_{1/2} = -0.370\text{V} - 0.0601\log[L]$$

From Equation 11.4.16 we know that the slope is equal to –0.05916*p*/*n*. Using the slope and n = 2, we solve for *p* obtaining a value of 2.03 ≈ 2. The complex's stoichiometry, therefore, is ML_2. We also know, from Equation 11.4.16, that the *y*-intercept is equivalent to –

$(0.05916/n)\log\beta_p$. Solving for β_2 gives a formation constant of 3.2×10^{12}.

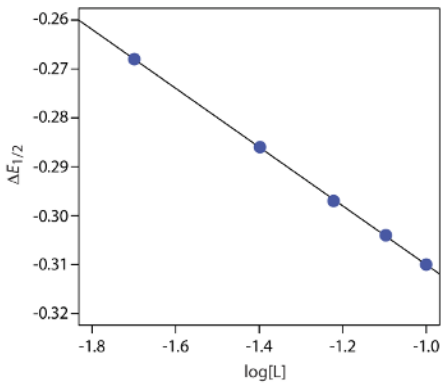


Figure 11.4.22 . Determination of the stoichiometry and formation constant for a metal-ligand complex using the data in Example 11.4.4 .

? EXERCISE 11.4.2

The voltammogram for 0.50 mM Cd^{2+} has an $E_{1/2}$ of –0.565 V versus an SCE. After making the solution 0.115 M in ethylenediamine, $E_{1/2}$ is –0.845 V, and $E_{1/2}$ is –0.873 V when the solution is 0.231 M in ethylenediamine. Determine the stoichiometry of the Cd^{2+}–ethylenediamine complex and its formation constant. The data in this problem comes from Morinaga, K. "Polarographic Studies of Metal Complexes. V. Ethylenediamine Complexes of Cadmium, Nickel, and Zinc," *Bull. Chem. Soc. Japan* **1956**, *29*, 793–799.

Answer

For simplicity, we will use *en* as a shorthand notation for ethylenediamine. From the three half-wave potentials we have a $\Delta E_{1/2}$ of –0.280 V for 0.115 M en and a $\Delta E_{1/2}$ of –0.308 V for 0.231 M en. Using Equation 11.4.16 we write the following two equations.

$$-0.280 = -\frac{0.05916}{2}\log\beta_p - \frac{0.05916p}{2}\log(0.115)$$
$$-0.308 = -\frac{0.05916}{2}\log\beta_p - \frac{0.05916p}{2}\log(0.231)$$

To solve for the value of *p*, we first subtract the second equation from the first equation

$$0.028 = -\frac{0.05916p}{2}\log(0.115) - \left\{-\frac{0.05916p}{2}\log(0.231)\right\}$$

which eliminates the term with β_p. Next we solve this equation for *p*

$$0.028 = \left(2.778 \times 10^{-2}\right) \times p - \left(1.882 \times 10^{-2}\right) \times p = \left(8.96 \times 10^{-3}\right) \times p$$

obtaining a value of 3.1, or $p \approx 3$. Thus, the complex is $Cd(en)_3$. To find the formation complex, β_3, we return to Equation 11.4.16, using our value for *p*. Using the data for an en concentration of 0.115 M

$$-0.280 = -\frac{0.05916}{2}\log\beta_3 - \frac{0.05916 \times 3}{2}\log(0.115)$$
$$-0.363 = -\frac{0.05916}{2}\log\beta_3$$

gives a value for β_3 of 1.92×10^{12}. Using the data for an en concentration of 0.231 M gives a value of 2.10×10^{12}.

As suggested by Figure 11.4.15 , cyclic voltammetry is one of the most powerful electrochemical techniques for exploring the mechanism of coupled electrochemical and chemical reactions. The treatment of this aspect of cyclic voltammetry is beyond the level of this text, although you can consult this chapter's additional resources for additional information.

EVALUATION

SCALE OF OPERATION

Detection levels at the parts-per-million level are routine. For some analytes and for some voltammetric techniques, lower detection limits are possible. Detection limits at the parts-per-billion and the part-per-trillion level are possible with stripping voltammetry. Although most analyses are carried out in conventional electrochemical cells using macro samples, the availability of microelectrodes with diameters as small as 2 μm, allows for the analysis of samples with volumes under 50 μL. For example, the concentration of glucose in 200-μm pond

snail neurons was monitored successfully using an amperometric glucose electrode with a 2 mm tip [Abe, T.; Lauw, L. L.; Ewing, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 7421–7423].

ACCURACY

The accuracy of a voltammetric analysis usually is limited by our ability to correct for residual currents, particularly those due to charging. For an analyte at the parts-per-million level, an accuracy of ±1–3% is routine. Accuracy decreases for samples with significantly smaller concentrations of analyte.

PRECISION

Precision generally is limited by the uncertainty in measuring the limiting current or the peak current. Under most conditions, a precision of ±1–3% is reasonable. One exception is the analysis of ultratrace analytes in complex matrices by stripping voltammetry, in which the precision may be as poor as ±25%.

SENSITIVITY

In many voltammetric experiments, we can improve the sensitivity by adjusting the experimental conditions. For example, in stripping voltammetry we can improve sensitivity by increasing the deposition time, by increasing the rate of the linear potential scan, or by using a differential-pulse technique. One reason that potential pulse techniques are popular is that they provide an improvement in current relative to a linear potential scan.

SELECTIVITY

Selectivity in voltammetry is determined by the difference between half-wave potentials or peak potentials, with a minimum difference of ±0.2–0.3 V for a linear potential scan and ±0.04–0.05 V for differential pulse voltammetry. We often can improve selectivity by adjusting solution conditions. The addition of a complexing ligand, for example, can substantially shift the potential where a species is oxidized or reduced to a potential where it no longer interferes with the determination of an analyte. Other solution parameters, such as pH, also can be used to improve selectivity.

TIME, COST, AND EQUIPMENT

Commercial instrumentation for voltammetry ranges from <$1000 for simple instruments to >$20,000 for a more sophisticated instrument. In general, less expensive instrumentation is limited to linear potential scans. More expensive instruments provide for more complex potential-excitation signals using potential pulses. Except for stripping voltammetry, which needs a long deposition time, voltammetric analyses are relatively rapid.

11.5: PROBLEMS

1. Identify the anode and the cathode for the following electrochemical cells, and identify the oxidation or the reduction reaction at each electrode.

(a) Pt| $FeCl_2$ (*aq*, 0.015), $FeCl_3$ (*aq*, 0.045) || $AgNO_3$ (*aq*, 0.1) | Ag

(b) Ag | AgBr(*s*), NaBr (*aq*, 1.0) || $CdCl_2$ (*aq*, 0.05) | Cd

(c) Pb | $PbSO_4$ (*s*), H_2SO_4 (*aq*, 1.5) || H_2SO_4 (*aq*, 2.0), $PbSO_4$ (*s*) | PbO_2

2. Calculate the potential for each electrochemical cell in problem 1. The values in parentheses are the activities of the associated species.

3. Calculate the activity of KI, *x*, in the following electrochemical cell if the potential is +0.294 V.

$$\text{Ag} \mid \text{AgCl}\ (s), \text{NaCl}\ (aq, 0.1) \parallel \text{KI}\ (\text{aq}, x), \text{I}_2\ (s) \mid \text{Pt}$$

4. What reaction prevents us from using Zn as an electrode of the first kind in an acidic solution? Which other metals do you expect to behave in the same manner as Zn when immersed in an acidic solution?

5. Creager and colleagues designed a salicylate ion-selective electrode using a PVC membrane impregnated with tetraalkylammonium salicylate [Creager, S. E.; Lawrence, K. D.; Tibbets, C. R. *J. Chem. Educ.* **1995**, *72*, 274–276]. To determine the ion-selective electrode's selectivity coefficient for benzoate, they prepared a set of salicylate calibration standards in which the concentration of benzoate was held constant at 0.10 M. Using the following data, determine the value of the selectivity coefficient.

[salicylate] (M)	potential (mV)
1.0	20.2
$\mathbf{1.0 \times 10^{-1}}$	73.5
$\mathbf{1.0 \times 10^{-2}}$	126
$\mathbf{1.0 \times 10^{-3}}$	168
$\mathbf{1.0 \times 10^{-4}}$	182
$\mathbf{1.0 \times 10^{-5}}$	182
$\mathbf{1.0 \times 10^{-6}}$	177

What is the maximum acceptable concentration of benzoate if you plan to use this ion-selective electrode to analyze a sample that contains as little as 10^{-5} M salicylate with an accuracy of better than 1%?

6. Watanabe and co-workers described a new membrane electrode for the determination of cocaine, a weak base alkaloid with a pK_a of 8.64 [Watanabe, K.; Okada, K.; Oda, H.; Furuno, K.; Gomita, Y.; Katsu, T. *Anal. Chim. Acta* **1995**, *316*, 371–375]. The electrode's response for a fixed concentration of cocaine is independent of pH in the range of 1–8, but decreases sharply above a pH of 8. Offer an explanation for this pH dependency.

7. Figure 11.2.14 shows a schematic diagram for an enzyme electrode that responds to urea by using a gas-sensing NH_3 electrode to measure the amount of ammonia released following the enzyme's reaction with urea. In turn, the NH_3 electrode uses a pH electrode to monitor the change in pH due to the ammonia. The response of the urea electrode is given by equation 11.2.12. Beginning with equation 11.2.19, which gives the potential of a pH electrode, show that equation 11.2.12 for the urea electrode is correct.

8. Explain why the response of an NH_3-based urea electrode (Figure 11.2.14 and equation 11.2.12) is different from the response of a urea electrode in which the enzyme is coated on the glass membrane of a pH electrode (Figure 11.2.15 and equation 11.2.13).

9. A potentiometric electrode for HCN uses a gas-permeable membrane, a buffered internal solution of 0.01 M $KAg(CN)_2$, and a Ag_2S ISE electrode that is immersed in the internal solution. Consider the equilibrium reactions that take place within the internal solution and derive an equation that relates the electrode's potential to the concentration of HCN in the sample. To check your work, search on-line for US Patent 3859191 and consult Figure 2.

10. Mifflin and associates described a membrane electrode for the quantitative analysis of penicillin in which the enzyme penicillinase is immobilized in a polyacrylamide gel coated on the glass membrane of a pH electrode [Mifflin, T. E.; Andriano, K. M.; Robbins, W. B. *J. Chem. Educ.* **1984**, *61*, 638–639]. The following data were collected using a set of penicillin standards.

[penicillin] (M)	potential (mV)
1.0×10^{-2}	220
2.0×10^{-3}	204
1.0×10^{-3}	190
2.0×10^{-4}	153
1.0×10^{-4}	135
1.0×10^{-5}	96
1.0×10^{-6}	80

(a) Over what range of concentrations is there a linear response?

(b) What is the calibration curve's equation for this concentration range?

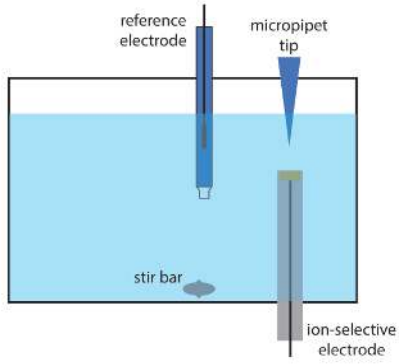
(c) What is the concentration of penicillin in a sample that yields a potential of 142 mV?

11. An ion-selective electrode can be placed in a flow cell into which we inject samples or standards. As the analyte passes through the cell, a potential spike is recorded instead of a steady-state potential. The concentration of K^+ in serum has been determined in this fashion using standards prepared in a matrix of 0.014 M NaCl [Meyerhoff, M. E.; Kovach, P. M. *J. Chem. Educ.* **1983**, *9*, 766–768].

$[K^+]$ (mM)	*E* (arb. units)	$[K^+]$ (mM)	*E* (arb. units)
0.10	25.5	0.60	58.7
0.20	37.2	0.80	64.0
0.40	50.8	1.00	66.8

A 1.00-mL sample of serum is diluted to volume in a 10-mL volumetric flask and analyzed, giving a potential of 51.1 (arbitrary units). Report the concentration of K^+ in the sample of serum.

12. Wang and Taha described an interesting application of potentiometry, which they call batch injection [Wang, J.; Taha, Z. *Anal. Chim. Acta* **1991**, *252*, 215–221]. As shown in the figure below, an ion-selective electrode is placed in an inverted position in a large volume tank, and a fixed volume of a sample or a standard solution is injected toward the electrode's surface using a micropipet. The response of the electrode is a spike in potential that is proportional to the analyte's concentration. The following data were collected using a pH electrode and a set of pH standards.



pH	potential (mV)
2.0	+300
3.0	+240
4.0	+168
5.0	+81
6.0	+35
8.0	–92
9.0	–168
10.0	–235
11.0	–279

Determine the pH of the following samples given the recorded peak potentials: tomato juice, 167 mV; tap water, –27 mV; coffee, 122 mV.

13. The concentration of NO_3^- in a water sample is determined by a one-point standard addition using a NO_3^- ion-selective electrode. A 25.00-mL sample is placed in a beaker and a potential of 0.102 V is measured. A 1.00-mL aliquot of a 200.0-mg/L standard solution of NO_3^- is added, after which the potential is 0.089 V. Report the mg NO_3^-/L in the water sample.

14. In 1977, when I was an undergraduate student at Knox College, my lab partner and I completed an experiment to determine the concentration of fluoride in tap water and the amount of fluoride in toothpaste. The data in this problem are from my lab notebook.

(a) To analyze tap water, we took three 25.0-mL samples and added 25.0 mL of TISAB to each. We measured the potential of each solution using a F^- ISE and an SCE reference electrode. Next, we made five 1.00-mL additions of a standard solution of 100.0 ppm F^- to each sample, and measured the potential after each addition, recording the potential three times.

mL of standard added	potential (mV), replicate 1	potential (mV), replicate 2	potential (mV), replicate 3
0.00	–79	–82	–83
1.00	–119	–119	–118
2.00	–133	–133	–133
3.00	–142	–142	–142
4.00	–149	–148	–148
5.00	–154	–153	–153

Report the parts-per-million of F^- in the tap water.

(b) To analyze the toothpaste, we measured 0.3619 g into a 100-mL volumetric flask, added 50.0 mL of TISAB, and diluted to volume with distilled water. After we ensured that the sample was thoroughly mixed, we transferred three 20.0-mL portions into separate beakers and measured the potential of each using a F^- ISE and an SCE reference electrode. Next, we made five 1.00-mL additions of a standard solution of 100.0 ppm F^- to each sample, and measured the potential after each addition, recording the potential three times.

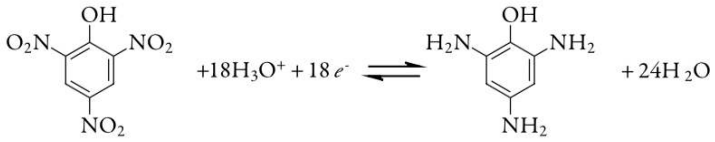
mL of standard added	potential (mV), replicate 1	potential (mV), replicate 2	potential (mV), replicate 3
0.00	–55	–54	–55
1.00	–82	–82	–83
2.00	–94	–94	–94
3.00	–102	–103	–102
4.00	–108	–108	–109
5.00	–112	–112	–113

Report the parts-per-million F^- in the toothpaste.

15. You are responsible for determining the amount of KI in iodized salt and decide to use an I^- ion-selective electrode. Describe how you would perform this analysis using external standards and how you would per-form this analysis using the method of standard additions.

16. Explain why each of the following decreases the analysis time in controlled-potential coulometry: a larger surface area for the working electrode; a smaller volume of solution; and a faster stirring rate.

17. The purity of a sample of picric acid, $C_6H_3N_3O_7$, is determined by controlled-potential coulometry, converting picric acid to triaminophenol, $C_6H_9N_3O$.



A 0.2917-g sample of picric acid is placed in a 1000-mL volumetric flask and diluted to volume. A 10.00-mL portion of this solution is transferred to a coulometric cell and sufficient water added so that the Pt cathode is immersed. An exhaustive electrolysis of the sample requires 21.67 C of charge. Report the purity of the picric acid.

18. The concentration of H_2S in the drainage from an abandoned mine is determined by a coulometric titration using KI as a mediator and I_3^- as the titrant.

$$H_2S(aq) + I_3^-(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + 3I^-(aq) + S(s)$$

A 50.00-mL sample of water is placed in a coulometric cell, along with an excess of KI and a small amount of starch as an indicator. Electrolysis is carried out at a constant current of 84.6 mA, requiring 386 s to reach the starch end point. Report the concentration of H_2S in the sample in μg/mL.

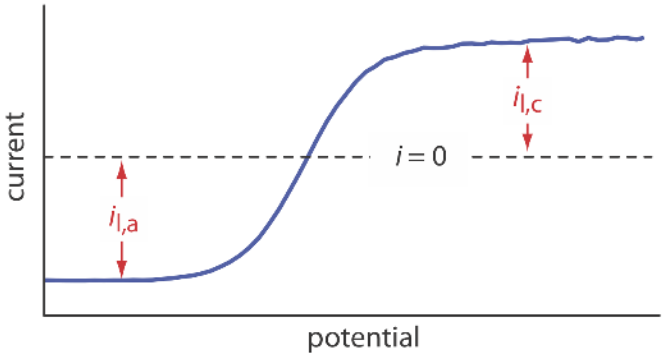
19. One method for the determination of a given mass of H_3AsO_3 is a coulometric titration using I_3^- as a titrant. The relevant standard-state reactions and potentials are summarized here

$$H_3AsO_4(aq) + 2H^+(aq) + 2e^- \rightleftharpoons H_3AsO_3(aq) + H_2O(l)$$
$$I_3^-(aq) + 2e^- \rightleftharpoons 3I^-(aq)$$

with standard state reduction potentials of, respectively, +0.559 V and +0.536 V. Explain why the coulometric titration is carried out in a neutral solution (pH ≈ 7) instead of in a strongly acidic solution (pH < 0).

20. The production of adiponitrile, $NC(CH_2)_4CN$, from acrylonitrile, CH_2=CHCN, is an important industrial process. A 0.594-g sample of acrylonitrile is placed in a 1-L volumetric flask and diluted to volume. An exhaustive controlled-potential electrolysis of a 1.00-mL portion of the diluted acrylonitrile requires 1.080 C of charge. What is the value of *n* for the reduction of acrylonitrile to adiponitrile?

21. The linear-potential scan hydrodynamic voltammogram for a mixture of Fe^{2+} and Fe^{3+} is shown in the figure below where $i_{l,a}$ and $i_{l,c}$ are the anodic and cathodic limiting currents.



(a) Show that the potential is given by

$$E = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916 \log \frac{K_{Fe^{3+}}}{K_{Fe^{2+}}} - 0.05916 \log \frac{i - i_{l,a}}{i_{l,c} - i}$$

(b) What is the potential when i = 0 for a solution that is 0.100 mM Fe^{3+} and 0.050 mM Fe^{2+}?

22. The amount of sulfur in aromatic monomers is determined by differential pulse polarography. Standard solutions are prepared for analysis by dissolving 1.000 mL of the purified monomer in 25.00 mL of an electrolytic solvent, adding a known amount of sulfur, deaerating, and measuring the peak current. The following results were obtained for a set of calibration standards.

μg S added	peak current (μA)
0	0.14
28	0.70
56	1.23
112	2.41
168	3.42

Analysis of a 1.000-mL sample, treated in the same manner as the standards, gives a peak current of 1.77 μA. Report the mg S/mL in the sample.

23. The purity of a sample of $K_3Fe(CN)_6$ is determined using linear-potential scan hydrodynamic voltammetry at a glassy carbon electrode. The following data were obtained for a set of external calibration standards.

$[K_3Fe(CN)_6]$ (mM)	limiting current (μA)
2.0	127
4.0	252
6.0	376
8.0	500
10.0	624

A sample of impure $K_3Fe(CN)_6$ is prepared for analysis by diluting a 0.246-g portion to volume in a 100-mL volumetric flask. The limiting current for the sample is 444 μA. Report the purity of this sample of $K_3Fe(CN)_6$.

24. One method for determining whether an individual recently fired a gun is to look for traces of antimony in residue collected from the individual's hands. Anodic stripping voltammetry at a mercury film electrode is ideally suited for this analysis. In a typical analysis a sample is collected from a suspect using a cotton-tipped swab wetted with 5% v/v HNO_3. After returning to the lab, the swab is placed in a vial that contains 5.0 mL of 4 M HCl that is 0.02 M in hydrazine sulfate. After soaking the swab, a 4.0-mL portion of the solution is transferred to an electrochemical cell along with 100 μL of 0.01 M $HgCl_2$. After depositing the thin film of mercury and the antimony, the stripping step gives a peak current of 0.38 μA. After adding a standard addition of 100 μL of $\mathbf{5.00 \times 10^2}$ ppb Sb, the peak current increases to 1.14 μA. How many nanograms of Sb were collected from the suspect's hand?

25. Zinc is used as an internal standard in an analysis of thallium by differential pulse polarography. A standard solution of $\mathbf{5.00 \times 10^{-5}}$ M Zn^{2+} and $\mathbf{2.50 \times 10^{-5}}$ M Tl^+ has peak currents of 5.71 μA and 3.19 μA, respectively. An 8.713-g sample of a zinc-free alloy is dissolved in acid, transferred to a 500-mL volumetric flask, and diluted to volume. A 25.0-mL portion of this solution is mixed with 25.0 mL of $\mathbf{5.00 \times 10^{-4}}$ M Zn^{2+}. Analysis of this solution gives peak currents of 12.3 μA and of 20.2 μA for Zn^{2+} and Tl^+, respectively. Report the %w/w Tl in the alloy.

26. Differential pulse voltammetry at a carbon working electrode is used to determine the concentrations of ascorbic acid and caffeine in drug formulations [Lau, O.; Luk, S.; Cheung, Y. *Analyst* **1989**, *114*, 1047–1051]. In a typical analysis a 0.9183-g tablet is crushed and ground into a fine powder. A 0.5630-g sample of this powder is transferred to a 100-mL volumetric flask, brought into solution, and diluted to volume. A 0.500-mL portion of this solution is then transferred to a voltammetric cell that contains 20.00 mL of a suitable supporting electrolyte. The resulting voltammogram gives peak currents of 1.40 μA and 3.88 μA for ascorbic acid and for caffeine, respectively. A 0.500-mL aliquot of a standard solution that contains 250.0 ppm ascorbic acid and 200.0 ppm caffeine is then added. A voltammogram of this solution gives peak currents of 2.80 μA and 8.02 μA for ascorbic acid and caffeine, respectively. Report the milligrams of ascorbic acid and milligrams of caffeine in the tablet.

27. Ratana-ohpas and co-workers described a stripping analysis method for determining tin in canned fruit juices [Ratana-ohpas, R.; Kanatharana, P.; Ratana-ohpas, W.; Kongsawasdi, W. *Anal. Chim. Acta* **1996**, *333*, 115–118]. Standards of 50.0 ppb Sn^{4+}, 100.0 ppb Sn^{4+}, and 150.0 ppb Sn^{4+} were analyzed giving peak currents (arbitrary units) of 83.0, 171.6, and 260.2, respectively. A 2.00-mL sample of lychee juice is mixed with 20.00 mL of 1:1 HCl/HNO_3. A 0.500-mL portion of this mixture is added to 10 mL of 6 M HCl and the volume adjusted to 30.00 mL. Analysis of this diluted sample gave a signal of 128.2 (arbitrary units). Report the parts-per-million Sn^{4+} in the original sample of lychee juice.

28. Sittampalam and Wilson described the preparation and use of an amperometric sensor for glucose [Sittampalam, G.; Wilson, G. S. *J. Chem. Educ.* **1982**, *59*, 70–73]. The sensor is calibrated by measuring the steady-state current when it is immersed in standard solutions of glucose. A typical set of calibration data is shown here.

[glucose] (mg/100 mL)	current (arb. units)
2.0	17.2
4.0	32.9
6.0	52.1
8.0	68.0
10.0	85.8

A 2.00-mL sample is diluted to 10 mL in a volumetric flask and a steady-state current of 23.6 (arbitrary units) is measured. What is the concentration of glucose in the sample in mg/100 mL?

29. Differential pulse polarography is used to determine the concentrations of lead, thallium, and indium in a mixture. Because the peaks for lead and thallium, and for thallium and indium overlap, a simultaneous analysis is necessary. Peak currents (in arbitrary units) at –0.385 V, –0.455 V, and –0.557 V are measured for a single standard solution, and for a sample, giving the results shown in the following table. Report the mg/mL of Pb^{2+}, Tl^+ and In^{3+} in the sample.

analyte	[standard] (μg/mL)	peak current at –0.385 V	peak current at –0.455 V	peak current at –0.557 V
Pb^{2+}	1.0	26.1	2.9	0
Tl^{+}	2.0	7.8	23.5	3.2
In^{3+}	0.4	0	0	22.9
	sample	60.6	28.8	54.1

30. Abass and co-workers developed an amperometric biosensor for NH_4^+ that uses the enzyme glutamate dehydrogenase to catalyze the following reaction

$$\text{2 - oxyglutarate } (aq) + NH_4^+(aq) + NADH(aq) \rightleftharpoons \text{ glutamate } (aq) + NAD^+(aq) + H_2O(l)$$

where NADH is the reduced form of nicotinamide adenine dinucleotide [Abass, A. K.; Hart, J. P.; Cowell, D. C.; Chapell, A. *Anal. Chim. Acta* **1988**, *373*, 1–8]. The biosensor actually responds to the concentration of NADH, however, the rate of the reaction depends on the concentration of NH_4^+. If the initial concentrations of 2-oxyglutarate and NADH are the same for all samples and standards, then the signal is proportional to the concentration of NH_4^+. As shown in the following table, the sensitivity of the method is dependent on pH.

pH	sensitivity (nA S^{-1} M^{-1})
6.2	1.67×10^3
6.75	5.00×10^3
7.3	9.33×10^3
7.7	1.04×10^4
8.3	1.27×10^4
9.3	2.67×10^3

Two possible explanations for the effect of pH on the sensitivity of this analysis are the acid–base chemistry of NH_4^+ and the acid–base chemistry of the enzyme. Given that the pK_a for NH_4^+ is 9.244, explain the source of this pH-dependent sensitivity.

31. The speciation scheme for trace metals in Table 11.4.2 divides them into seven operationally defined groups by collecting and analyzing two samples following each of four treatments, requiring a total of eight samples and eight measurements. After removing insoluble particulates by filtration (treatment 1), the solution is analyzed for the concentration of ASV labile metals and for the total concentration of metals. A portion of the filtered solution is then passed through an ion-exchange column (treatment 2), and the concentrations of ASV metal and of total metal are determined. A second portion of the filtered solution is irradiated with UV light (treatment 3), and the concentrations of ASV metal and of total metal are measured. Finally, a third portion of the filtered solution is irradiated with UV light and passed through an ion-exchange column (treatment 4), and the concentrations of ASV labile metal and of total metal again are determined. The groups that are included in each measurement are summarized in the following table.

treatment	groups removed by treatement	groups contributing to ASV-labile metals	groups contributing to total metals
1	none	I, II, III	I, II, III, IV, V, VI, VII
2	I, IV, V	II, III	II, III, V1, VII
3	none	I, II, III, IV, VI	I, II, III, IV, V, VI, VII
4	I, II, IV, V, VI	III	III, VII

(a) Explain how you can use these eight measurements to determine the concentration of metals present in each of the seven groups identified in Table 11.4.2.

(b) Batley and Florence report the following results for the speciation of cadmium, lead, and copper in a sample of seawater [Batley, G. E.; Florence, T. M. *Anal. Lett.* **1976**, *9*, 379–388]. Determine the speciation of each metal in comment on your results.

measurement treatement: ASV-labile or total	ppb Cd^{2+}	ppb Pb^{2+}	ppb Cu^{2+}
1: ASV-labile	0.24	0.39	0.26
2: total	0.28	0.50	0.40
2: ASV-labile	0.21	0.33	0.17
2: total	0.26	0.43	0.24
3: ASV-labile	0.26	0.37	0.33
3: total	0.28	0.5	0.43
4: ASV-labile	0.00	0.00	0.00
4: total	0.02	0.12	0.10

32. The concentration of Cu^{2+} in seawater is determined by anodic stripping voltammetry at a hanging mercury drop electrode after first releasing any copper bound to organic matter. To a 20.00-mL sample of seawater is added 1 mL of 0.05 M HNO_3 and 1 mL of 0.1% H_2O_2. The sample is irradiated with UV light for 8 hr and then diluted to volume in a 25-mL volumetric flask. Deposition of Cu^{2+} takes place at –0.3 V versus an SCE for 10 min, producing a peak current of 26.1 (arbitrary units). A second 20.00-mL sample of the seawater is treated identically, except that 0.1 mL of a 5.00 μM solution of Cu^{2+} is added, producing a peak current of 38.4 (arbitrary units). Report the concentration of Cu^{2+} in the seawater in mg/L.

33. Thioamide drugs are determined by cathodic stripping analysis [Davidson, I. E.; Smyth, W. F. Anal. Chem. 1977, 49, 1195–1198]. Deposition occurs at +0.05 V versus an SCE. During the stripping step the potential is scanned cathodically and a stripping peak is observed at –0.52 V. In a typical application a 2.00-mL sample of urine is mixed with 2.00 mL of a pH 4.78 buffer. Following a 2.00 min deposition, a peak current of 0.562 μA is measured. A 0.10-mL addition of a 5.00 μM solution of the drug is added to the same solution. A peak current of 0.837 μA is recorded using the same deposition and stripping conditions. Report the drug's molar concentration in the urine sample.

34. The concentration of vanadium (V) in sea water is determined by adsorptive stripping voltammetry after forming a complex with catechol [van der Berg, C. M. G.; Huang, Z. Q. *Anal. Chem.* **1984**, *56*, 2383–2386]. The catechol-V(V) complex is deposited on a hanging mercury drop electrode at a potential of –0.1 V versus a Ag/AgCl reference electrode. A cathodic potential scan gives a stripping peak that is proportional to the concentration of V(V). The following standard additions are used to analyze a sample of seawater.

$[V(V)]_{added}$ (M)	peak current (μA)
2.0×10^{-8}	24
4.0×10^{-8}	33
8.0×10^{-8}	52
1.2×10^{-7}	69
1.8×10^{-7}	97
2.8×10^{-7}	140

Determine the molar concentration of V (V) in the sample of sea water, assuming that the standard additions result in a negligible change in the sample's volume.

35. The standard-state reduction potential for Cu^{2+} to Cu is +0.342 V versus the SHE. Given that Cu^{2+} forms a very stable complex with the ligand EDTA, do you expect that the standard-state reduction potential for $Cu(EDTA)^{2-}$ is greater than +0.342 V, less than +0.342 V, or equal to +0.342 V? Explain your reasoning.

36. The polarographic half-wave potentials (versus the SCE) for Pb^{2+} and for Tl^{+} in 1 M HCl are, respectively, –0.44 V and –0.45 V. In an electrolyte of 1 M NaOH, however, the half-wave potentials are –0.76 V for Pb^{2+} and –0.48 V for Tl^{+}. Why does the change in electrolyte have such a significant effect on the half-wave potential for Pb^{2+}, but not on the half-wave potential for Tl^{+}?

37. The following data for the reduction of Pb^{2+} were collected by normal-pulse polarography.

potential (V vs. SCE)	current (μA)
–0.345	0.16
–0.370	0.98
–0.383	2.05
–0.393	3.13
–0.409	4.62
–0.420	5.16

The limiting current was 5.67 μA. Verify that the reduction reaction is reversible and determine values for n and $E_{1/2}$. The half-wave potentials for the normal-pulse polarograms of Pb^{2+} in the presence of several different concentrations of OH^- are shown in the following table.

$[OH^-]$ (M)	$E_{1/2}$ (V vs. SCE)	$[OH^-]$ (M)	$E_{1/2}$ (V vs. SCE)
0.050	–0.646	0.150	–0.689
0.100	–0.673	0.300	–0.715

Determine the stoichiometry of the Pb-hydroxide complex and its formation constant.

38. In 1977, when I was an undergraduate student at Knox College, my lab partner and I completed an experiment to study the voltammetric behavior of Cd^{2+} (in 0.1 M KNO_3) and Ni^{2+} (in 0.2 M KNO_3) at a dropping mercury electrode. The data in this problem are from my lab notebook. All potentials are relative to an SCE reference electrode.

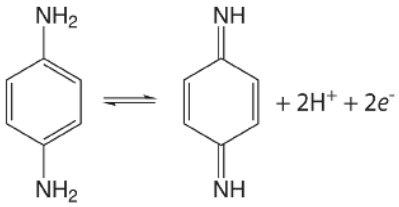
potential for Cd^{2+} (V)	current for Cd^{2+} (μA)	potential for Ni^{2+} (V)	current for Ni^{2+} (μA)
–0.60	4.5	–1.07	1.90
–0.58	3.4	–1.05	1.75
–0.56	2.1	–1.03	1.50
–0.54	0.6	–1.02	1.25
–0.52	0.2	–1.00	1.00

The limiting currents for Cd^{2+} was 4.8 μA and that for Ni^{2+} was 2.0 μA. Evaluate the electrochemical reversibility for each metal ion and comment on your results.

39. Baldwin and co-workers report the following data from a cyclic voltammetry study of the electrochemical behavior of *p*-phenylenediamine in a pH 7 buffer [Baldwin, R. P.; Ravichandran, K.; Johnson, R. K. *J. Chem. Educ.* **1984**, *61*, 820–823]. All potentials are measured relative to an SCE.

scan rate (mV/s)	$E_{p,a}$ (V)	$E_{p,c}$ (V)	$i_{p,a}$ (mA)	$i_{p,c}$ (mA)
2	0.148	0.104	0.34	0.30
5	0.149	0.098	0.56	0.53
10	0.152	0.095	1.00	0.04
20	0.161	0.095	1.44	1.44
50	0.167	0.082	2.12	1.81
100	0.180	0.063	2.50	2.19

The initial scan is toward more positive potentials, leading to the oxidation reaction shown here.



Use this data to show that the reaction is electrochemically irreversible. A reaction may show electrochemical irreversibility because of slow electron transfer kinetics or because the product of the oxidation reaction participates in a chemical reaction that produces an nonelectroactive species. Based on the data in this problem, what is the likely source of *p*-phenylenediamine's electrochemical irreversibility?

11.6: ADDITIONAL RESOURCES

The following set of experiments introduce students to the applications of electrochemistry. Experiments are grouped into four categories: general electrochemistry, preparation of electrodes, potentiometry, coulometry, and voltammetry and amperometry.

General Electrochemistry

- Chatmontree, A.; Chairam, S.; Supasorn, S.; Amatatongchai, M.; Jarujamrus, P; Tamuang, S.; Somsook E. "Student Fabriaction and Use of Simple, Low-Cost, Paper-Based Galvanic Cells to Investigate Electrochemistry," *J. Chem. Educ.* **2015**, *92*, 1044–1048.
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Preparation of Electrodes

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Potentiometry

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Coulometry

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11.7: CHAPTER SUMMARY AND KEY TERMS

CHAPTER SUMMARY

In this chapter we introduced three electrochemical methods of analysis: potentiometry, coulometry, and voltammetry. In potentiometry we measure the potential at an indicator electrode without allowing any significant current to pass through the electrochemical cell, and use the Nernst equation to calculate the analyte's activity after accounting for junction potentials.

There are two broad classes of potentiometric electrodes: metallic electrodes and membrane electrodes. The potential of a metallic electrode is the result of a redox reaction at the electrode's surface. An electrode of the first kind responds to the concentration of its cation in solution; thus, the potential of a Ag wire is determined by the activity of Ag^+ in solution. If another species is in equilibrium with the metal ion, the electrode's potential also responds to the concentration of that species. For example, the potential of a Ag wire in a solution of $Cl^–$ responds to the concentration of $Cl^–$ because the relative concentrations of Ag^+ and $Cl^–$ are fixed by the solubility product for AgCl. We call this an electrode of the second kind.

The potential of a membrane electrode is determined by a difference in the composition of the solution on each side of the membrane. Electrodes that use a glass membrane respond to ions that bind to negatively charged sites on the membrane's surface. A pH electrode is one example of a glass membrane electrode. Other kinds of membrane electrodes include those that use insoluble crystalline solids or liquid ion-exchangers incorporated into a hydrophobic membrane. The $F^–$ ion-selective electrode, which uses a single crystal of LaF_3 as the ion-selective membrane, is an example of a solid-state electrode. The Ca^{2+} ion-selective electrode, in which the chelating ligand di-(*n*-decyl)phosphate is immobilized in a PVC membrane, is an example of a liquid-based ion-selective electrode.

Potentiometric electrodes are designed to respond to molecules by using a chemical reaction that produces an ion whose concentration is determined using a traditional ion-selective electrode. A gas-sensing electrode, for example, includes a gas permeable membrane that isolates the ion-selective electrode from the gas. When a gas-phase analyte diffuses across the membrane it alters the composition of the inner solution, which is monitored with an ion-selective electrode. An enzyme electrodes operate in the same way.

Coulometric methods are based on Faraday's law that the total charge or current passed during an electrolysis is proportional to the amount of reactants and products participating in the redox reaction. If the electrolysis is 100% efficient—which means that only the analyte is oxidized or reduced—then we can use the total charge or total current to determine the amount of analyte in a sample. In controlled-potential coulometry we apply a constant potential and measure the resulting current as a function of time. In controlled-current coulometry the current is held constant and we measure the time required to completely oxidize or reduce the analyte.

In voltammetry we measure the current in an electrochemical cell as a function of the applied potential. There are several different voltammetric methods that differ in terms of the choice of working electrode, how we apply the potential, and whether we include convection (stirring) as a means for transporting of material to the working electrode.

Polarography is a voltammetric technique that uses a mercury electrode and an unstirred solution. Normal polarography uses a dropping mercury electrode, or a static mercury drop electrode, and a linear potential scan. Other forms of polarography include normal pulse polarography, differential pulse polarography, staircase polarography, and square-wave polarography, all of which use a series of potential pulses.

In hydrodynamic voltammetry the solution is stirred using either a magnetic stir bar or by rotating the electrode. Because the solution is stirred a dropping mercury electrode is not used; instead we use a solid electrode. Both linear potential scans and potential pulses can be applied.

In stripping voltammetry the analyte is deposited on the electrode, usually as the result of an oxidation or reduction reaction. The potential is then scanned, either linearly or using potential pulses, in a direction that removes the analyte by a reduction or oxidation reaction.

Amperometry is a voltammetric method in which we apply a constant potential to the electrode and measure the resulting current. Amperometry is most often used in the construction of chemical sensors for the quantitative analysis of single analytes. One important example is the Clark O_2 electrode, which responds to the concentration of dissolved O_2 in solutions such as blood and water.

KEY TERMS

amalgam
amperometry
anode
anodic current
asymmetry potential
auxiliary electrode
cathode
cathodic current
charging current
controlled-current coulometry
controlled-potential coulometry
convection
coulometric titrations
coulometry
counter electrode
current efficiency
cyclic voltammetry
diffusion
diffusion layer
dropping mercury electrode
electrical double layer
electrochemically irreversible
electrochemically reversible
electrode of the first kind
electrode of the second kind
electrochemistry
electrogravimetry
enzyme electrodes
faradaic current
Faraday's law
galvanostat
gas-sensing electrode
glass electrode
hanging mercury drop electrode
hydrodynamic voltammetry
indicator electrode
ionophore
ion selective electrode
junction potential
limiting current
liquid-based ion-selective electrode
mass transport
mediator
membrane potential
mercury film electrode
migration
nonfaradaic current
Ohm's law
overpotential
peak current
polarography
potentiometer
potentiostat
pulse polarography
redox electrode
reference electrode
residual current
salt bridge
saturated calomel electrode
selectivity coefficient
silver/silver chloride electrode
solid-state ion-selective electrodes
standard hydrogen electrode
static mercury drop electrode
stripping voltammetry
total ionic strength adjustment buffer
voltammetry
voltammogram
working electrode