Potentiometry

CHAPTER 21

The research vessel *Meteor*, shown in the photo, is owned by the Federal Republic of Germany through the Ministry of Research and Technology and is operated by the German Research Foundation. It is used by a multinational group of chemical oceanographers to collect data in an effort to better understand the changing chemical composition of the earth's atmosphere and oceans. For example, during April, 2012, a group from the Uni Bjerknes Centre and the Bjerknes Centre for Climate Research in Bergen, Norway, were aboard *Meteor* in the North Atlantic Ocean west of Norway performing measurements related to the oceanic cycling of carbon as well as measurements estimating the flux of oxygen directly involved in biological activity. An important observation in these experiments is the total alkalinity of sea water, which is determined by potentiometric titration, a method that is discussed in this chapter.

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Potentiometric methods of analysis are based on measuring the potential of electrochemical cells without drawing appreciable current. For nearly a century, potentiometric techniques have been used for locating end points in titrations. In more recent methods, ion concentrations are measured directly from the potential of ion-selective membrane electrodes. These electrodes are relatively free from interferences and provide a rapid, convenient, and nondestructive means for quantitatively determining numerous important anions and cations.[1]

Analysts make more potentiometric measurements than perhaps any other type of chemical instrumental measurement. The number of potentiometric measurements made on a daily basis is staggering. Manufacturers measure the pH of many consumer products, clinical laboratories determine blood gases as important indicators of disease states, industrial and municipal effluents are monitored continuously to determine pH and concentrations of pollutants, and oceanographers determine carbon dioxide and other related variables in seawater. Potentiometric measurements are also used in fundamental studies to determine thermodynamic equilibrium constants, such as K_a, K_b, and K_{sp}. These examples are but a few of the many thousands of applications of potentiometric measurements.

The equipment for potentiometric methods is simple and inexpensive and includes a reference electrode, an indicator electrode, and a potential-measuring device. The principles of operation and design of each of these components are described in the initial sections of this chapter. Following these discussions, we investigate analytical applications of potentiometric measurements.

[1]R. S. Hutchins and L. G. Bachas, in *Handbook of Instrumental Techniques for Analytical Chemistry*, F. A. Settle, ed., Ch. 38, pp. 727–48, Upper Saddle River, NJ: Prentice-Hall, 1997.

21A GENERAL PRINCIPLES

In Feature 18-3, we showed that absolute values for individual half-cell potentials cannot be determined in the laboratory, that is, only relative cell potentials can be measured experimentally. **Figure 21-1** shows a typical cell for potentiometric analysis. This cell can be represented as

$$\underbrace{\text{reference electrode}}_{E_{ref}}\,|\,\underbrace{\text{salt bridge}}_{E_j}\,|\,\text{analyte solution}\,|\,\underbrace{\text{indicator electrode}}_{E_{ind}}$$

A **reference electrode** is a half-cell having a known electrode potential that remains constant at constant temperature and is independent of the composition of the analyte solution.

An **indicator electrode** has a potential that varies in a known way with variations in the concentration of an analyte.

The **reference electrode** in this diagram is a half-cell with an accurately known electrode potential, E_{ref}, that is independent of the concentration of the analyte or any other ions in the solution under study. It can be a standard hydrogen electrode but seldom is because a standard hydrogen electrode is somewhat troublesome to maintain and use. By convention, the reference electrode is always treated as the left-hand electrode in potentiometric measurements. The **indicator electrode**, which is immersed in a solution of the analyte, develops a potential, E_{ind}, that depends on the activity of the analyte. Most indicator electrodes used in potentiometry are selective in their responses. The third component of a potentiometric cell is a salt bridge that prevents the components of the analyte solution from mixing with those of the reference electrode. As noted in Chapter 18, a potential develops across the liquid junctions at each end of the salt bridge. These two potentials tend to cancel one another if the mobilities of the cation and the anion in the bridge solution are approximately the same. Potassium chloride is a nearly ideal electrolyte for the salt bridge because the mobilities of the K^+ ion and the Cl^- ion are nearly equal. The net potential across the salt bridge, E_j, is thereby reduced to a few millivolts or less. For most electroanalytical methods, the junction potential is small enough to be neglected. In the potentiometric methods discussed in this chapter, however, the junction potential and its uncertainty can be factors that limit the measurement accuracy and precision.

As shown in Figure 21-1, reference electrodes are *always* treated as the left-hand electrode. This practice, which we adopt throughout this text, is consistent with the International Union of Pure and Applied Chemistry (IUPAC) convention for electrode potentials, discussed in Section 18C-4, in which the reference is the standard hydrogen electrode and is the electrode on the left in a cell diagram.

A hydrogen electrode is seldom used as a reference electrode for day-to-day potentiometric measurements because it is inconvenient to use and maintain and is also a fire hazard.

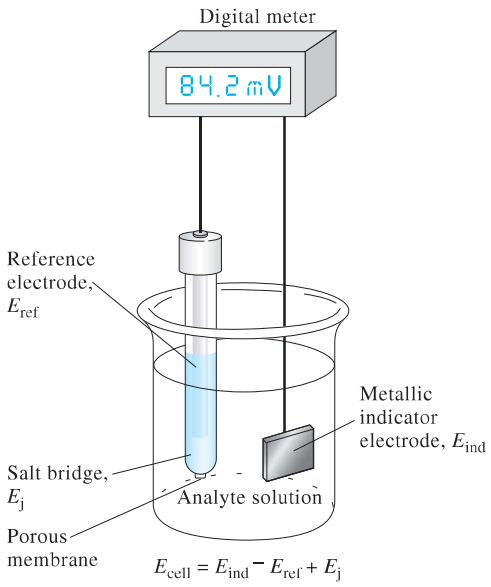


Figure 21-1 A cell for potentiometric determinations.

The potential of the cell we have just considered is given by the equation

$$E_{cell} = E_{ind} - E_{ref} + E_j \qquad (21\text{-}1)$$

The first term in this equation, E_{ind}, contains the information that we are looking for—the concentration of the analyte. To make a potentiometric determination of an analyte then, we must measure a cell potential, correct this potential for the reference and junction potentials, and compute the analyte concentration from the indicator electrode potential. Strictly, the potential of a galvanic cell is related to the activity of the analyte. Only through proper calibration of the electrode system with solutions of known concentration can we determine the concentration of the analyte.

In the sections that follow, we discuss the nature and origin of the three potentials shown on the right side of Equation 21-1.

21B REFERENCE ELECTRODES

The ideal reference electrode has a potential that is accurately known, constant, and completely insensitive to the composition of the analyte solution. In addition, this electrode should be rugged, easy to assemble, and should maintain a constant potential while passing minimal currents.

21B-1 Calomel Reference Electrodes

Calomel reference electrodes consist of mercury in contact with a solution that is saturated with mercury(I) chloride (calomel) and that also contains a known concentration of potassium chloride. Calomel half-cells can be represented as follows:

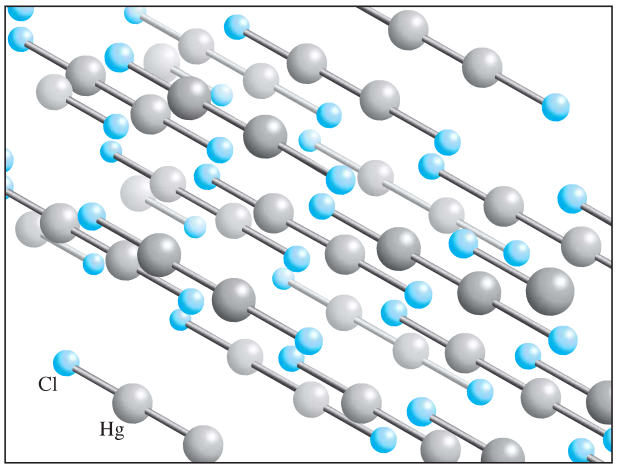
$$Hg\,|\,Hg_2Cl_2(\text{sat'd}),\ KCl(x\ M)\,\|$$

where x represents the molar concentration of potassium chloride in the solution. The electrode potential for this half-cell is determined by the reaction

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

and depends on the chloride concentration. Thus, the KCl concentration must be specified in describing the electrode.

The "saturated" in a saturated calomel electrode refers to the KCl concentration and not the calomel concentration. All calomel electrodes are saturated with Hg_2Cl_2 (calomel).



The crystal structure of calomel, Hg_2Cl_2, which has a limited solubility in water ($K_{sp} = 1.8 \times 10^{-18}$ at 25°C). Notice the Hg—Hg bond in the structure. There is considerable evidence that a similar type of bonding occurs in aqueous solution, and so mercury(I) is represented as Hg_2^{2+}.

TABLE 21-1

Formal Electrode Potentials for Reference Electrodes as a Function of Composition and Temperature

	Potential versus SHE, V				
Temperature, °C	0.1 M Calomel*	3.5 M Calomel†	Sat'd Calomel*	3.5 M Ag/AgCl†	Sat'd Ag/AgCl†
15	0.3362	0.254	0.2511	0.212	0.209
20	0.3359	0.252	0.2479	0.208	0.204
25	0.3356	0.250	0.2444	0.205	0.199
30	0.3351	0.248	0.2411	0.201	0.194
35	0.3344	0.246	0.2376	0.197	0.189

*From R. G. Bates, in *Treatise on Analytical Chemistry*, 2nd ed., I. M. Kolthoff and P. J. Elving, eds., Part I, Vol. 1, p. 793, New York: Wiley, 1978.
†From D. T. Sawyer, A. Sobkowiak, and J. L. Roberts, Jr., *Electrochemistry for Chemists*, New York: Wiley, 1995, p. 192.

A salt bridge is easily constructed by filling a U-tube with a conducting gel prepared by heating about 5 g of agar in 100 mL of an aqueous solution containing about 35 g of potassium chloride. When the liquid cools, it sets up into a gel that is a good conductor but prevents the two solutions at the ends of the tube from mixing. If either of the ions in potassium chloride interfere with the measurement process, ammonium nitrate may be used as the electrolyte in salt bridges.

Agar, which is available as translucent flakes, is a heteropolysaccharide that is extracted from certain East Indian seaweed. Solutions of agar in hot water set to a gel when they are cooled.

Table 21-1 lists the compositions and formal electrode potentials for the three most common calomel electrodes. Note that each solution is saturated with mercury(I) chloride (calomel) and that the cells differ only with respect to the potassium chloride concentration. Several convenient calomel electrodes, such as the electrode illustrated in **Figure 21-2**, are available commercially. The H-shape body of the electrode is made of glass of dimensions shown in the diagram. The right arm of the electrode contains a platinum electrical contact, a small quantity of mercury/mercury(I) chloride paste in saturated potassium chloride, and a few crystals of KCl. The tube is filled with saturated KCl to act as a salt bridge (see Section 18B-2) through a piece of porous Vycor ("thirsty glass") sealed in the end of the left arm. This type of junction has a relatively high resistance (2000 to 3000 Ω) and a limited current-carrying capacity, but contamination of the analyte solution due to leakage of potassium chloride is minimal. Other configurations of SCEs are available with much lower resistance and better electrical contact to the analyte solution, but they tend to leak small amounts of saturated potassium chloride into the sample. Because of concerns with mercury contamination, SCEs are less common than they once were, but for some applications, they are superior to Ag-AgCl reference electrodes, which are described next.

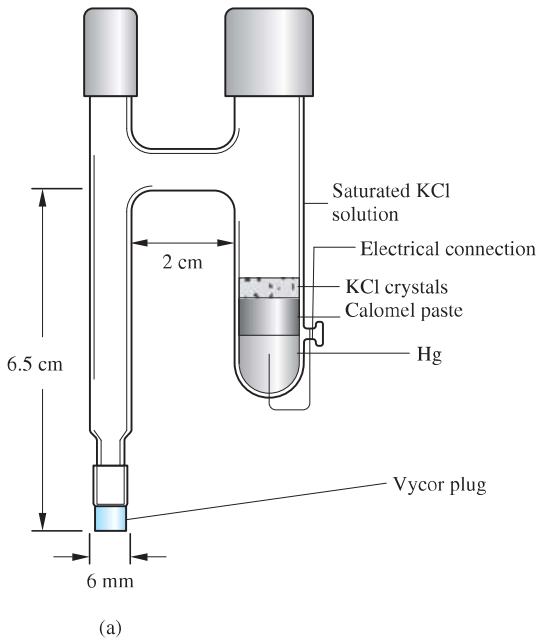


Figure 21-2 Diagram of a typical commercial saturated calomel electrode. (Reprinted with permission of Bioanalytical Systems, W. Lafayette, IN.)

21B-2 Silver/Silver Chloride Reference Electrodes

The most widely marketed reference electrode system consists of a silver electrode immersed in a solution of potassium chloride that has been saturated with silver chloride:

$$\text{Ag}|\text{AgCl(sat'd), KCl(sat'd)}\|$$

At 25°C, the potential of the saturated calomel electrode versus the standard hydrogen electrode is 0.244 V. For the saturated silver/silver chloride electrode, it is 0.199 V.

The electrode potential is determined by the half-reaction

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

Normally, this electrode is prepared with either a saturated or a 3.5 M potassium chloride solution; potentials for these electrodes are given in Table 21-1. **Figure 21-3** shows a commercial model of this electrode, which is little more than a piece of glass tubing that has a narrow opening at the bottom connected to a Vycor plug for making contact with the analyte solution. The tube contains a silver wire coated with a layer of silver chloride that is immersed in a potassium chloride solution saturated with silver chloride.

Silver–silver chloride electrodes have the advantage that they can be used at temperatures greater than 60°C, while calomel electrodes cannot. On the other hand, mercury(II) ions react with fewer sample components than do silver ions (which can react with proteins, for example). Such reactions can lead to plugging of the junction between the electrode and the analyte solution.

21C LIQUID-JUNCTION POTENTIALS

When two electrolyte solutions of different composition are in contact with one another, there is a potential difference across the interface. This junction potential is the result of an unequal distribution of cations and anions across the boundary due

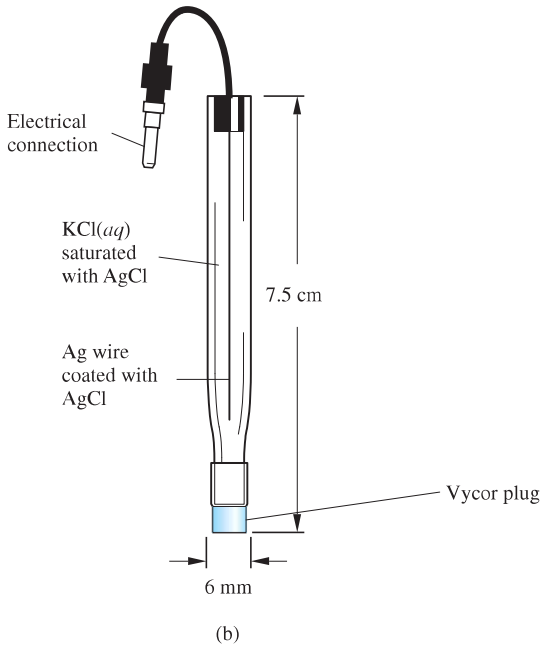


Figure 21-3 Diagram of a silver/silver chloride electrode showing the parts of the electrode that produce the reference electrode potential, E_{ref}, and the junction potential, E_j. (Reprinted with permission of Bioanalytical Systems, W. Lafayette, IN.)

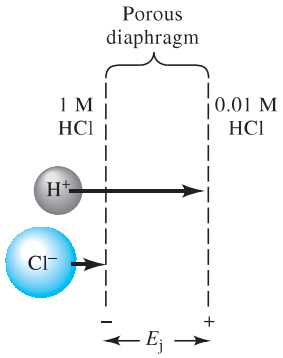


Figure 21-4 Schematic representation of a liquid junction, showing the source of the junction potential, E_j. The lengths of the arrows correspond to the relative mobilities of the ions.

to differences in the rates at which these species diffuse. **Figure 21-4** shows a very simple liquid junction consisting of a 1 M hydrochloric acid solution that is in contact with a solution that is 0.01 M in that acid. An inert porous barrier, such as a fritted glass plate, prevents the two solutions from mixing. The liquid junction may be represented as

$$\text{HCl(1 M)}|\text{HCl(0.01 M)}$$

Both hydrogen ions and chloride ions tend to diffuse across this boundary from the more concentrated to the more dilute solution, that is, left to right. The driving force for each ion is proportional to the activity difference between the two solutions. In the present example, hydrogen ions are substantially more mobile than chloride ions. Thus, hydrogen ions diffuse more rapidly than chloride ions, and as shown in the Figure 21-4, a separation of charge results. The more dilute side of the boundary becomes positively charged because of the more rapid diffusion of hydrogen ions. The concentrated side, therefore, acquires a negative charge from the excess of slower-moving chloride ions. The charge developed tends to counteract the differences in diffusion rates of the two ions so that a condition of equilibrium is attained rapidly. The potential difference resulting from this charge separation may be several hundredths of a volt.

The junction potential across a typical KCl salt bridge is a few millivolts. ❯

The magnitude of the liquid-junction potential can be minimized by placing a salt bridge between the two solutions. The salt bridge is most effective if the mobilities of the negative and positive ions in the bridge are nearly equal and if their concentrations are large. A saturated solution of potassium chloride is good from both standpoints. The junction potential with such a bridge is typically a few millivolts.

21D INDICATOR ELECTRODES

The results of potentiometric determinations are the activities of analytes in contrast to most analytical methods that give the concentrations of analytes. Recall that the activity of a species a_X is related to the molar concentration of X by Equation 10-2

$$a_X = \gamma_X[X]$$

where γ_X is the activity coefficient of X, a parameter that varies with the ionic strength of the solution. Because potentiometric data are dependent on activities, it will not be necessary in most cases to make the usual approximation that $a_X \approx [X]$ in this chapter. ❯

An ideal indicator electrode responds rapidly and reproducibly to changes in the concentration of an analyte ion (or group of analyte ions). Although no indicator electrode is absolutely specific in its response, a few are now available that are remarkably selective. Indicator electrodes are of three types: metallic, membrane, and ion-sensitive field effect transistors.

21D-1 Metallic Indicator Electrodes

It is convenient to classify metallic indicator electrodes as **electrodes of the first kind**, **electrodes of the second kind**, and **inert redox electrodes**.

Electrodes of the First Kind

An electrode of the first kind is a pure metal electrode that is in direct equilibrium with its cation in the solution. A single reaction is involved. For example, the equilibrium between a copper and its cation Cu^{2+} is

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

for which

$$E_{ind} = E^0_{Cu} - \frac{0.0592}{2}\log\frac{1}{a_{Cu^{2+}}} = E^0_{Cu} + \frac{0.0592}{2}\log a_{Cu^{2+}} \qquad (21\text{-}2)$$

where E_{ind} is the electrode potential of the metal electrode and $a_{Cu^{2+}}$ is the activity of the ion (or in dilute solution, approximately its molar concentration, $[Cu^{2+}]$).

We often express the electrode potential of the indicator electrode in terms of the p-function of the cation ($pX = -\log a_{Cu^{2+}}$). Thus, substituting this definition of pCu into Equation 21-2 gives

$$E_{ind} = E^0_{Cu} + \frac{0.0592}{2}\log a_{Cu^{2+}} = E^0_{Cu} - \frac{0.0592}{2}pCu$$

A general expression for any metal and its cation is

$$E_{ind} = E^0_{X^{n+}/X} + \frac{0.0592}{n}\log a_{X^{n+}} = E^0_{X^{n+}/X} - \frac{0.0592}{n}pX \qquad (21\text{-}3)$$

This function is plotted in **Figure 21-5**.

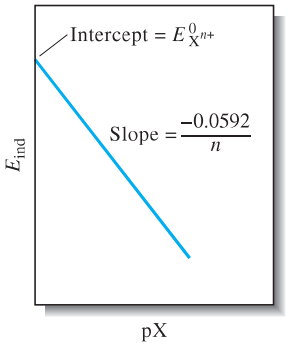


Figure 21-5 A plot of Equation 21-3 for an electrode of the first kind.

Electrode systems of the first kind are not widely used for potentiometric determinations for several reasons. For one, metallic indicator electrodes are not very selective and respond not only to their own cations but also to other more easily reduced cations. For example, a copper electrode cannot be used for the determination of copper(II) ions in the presence of silver(I) ions because the electrode potential is also a function of the Ag^+ concentration. In addition, many metal electrodes, such as zinc and cadmium, can only be used in neutral or basic solutions because they dissolve in the presence of acids. Third, other metals are so easily oxidized that they can be used only when analyte solutions are deaerated to remove oxygen. Finally, certain harder metals, such as iron, chromium, cobalt, and nickel, do not provide reproducible potentials. For these electrodes, plots of E_{ind} versus pX yield slopes that differ significantly and irregularly from the theoretical ($-0.0592/n$). For these reasons, the only electrode systems of the first kind that have been used in potentiometry are Ag/Ag^+ and Hg/Hg^{2+} in neutral solutions and Cu/Cu^{2+}, Zn/Zn^{2+}, Cd/Cd^{2+}, Bi/Bi^{3+}, Tl/Tl^+, and Pb/Pb^{2+} in deaerated solutions.

Electrodes of the Second Kind

Metals not only serve as indicator electrodes for their own cations but also respond to the activities of anions that form sparingly soluble precipitates or stable complexes with such cations. The potential of a silver electrode, for example, correlates reproducibly with the activity of chloride ion in a solution saturated with silver chloride. In this situation, the electrode reaction can be written as

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq) \qquad E^0_{AgCl/Ag} = 0.222\ V$$

The Nernst expression for this process at 25°C is

$$E_{ind} = E^0_{AgCl/Ag} - 0.0592\log a_{Cl^-} = E^0_{AgCl/Ag} + 0.0592\ pCl \qquad (21\text{-}4)$$

Equation 21-4 shows that the potential of a silver electrode is proportional to pCl, the negative logarithm of the chloride ion activity. Thus, in a solution saturated with silver chloride, a silver electrode can serve as an indicator electrode of the second kind for chloride ion. Note that the sign of the log term for an electrode of this type is opposite that for an electrode of the first kind (see Equation 21-3). A plot of the potential of the silver electrode versus pCl is shown in **Figure 21-6**.

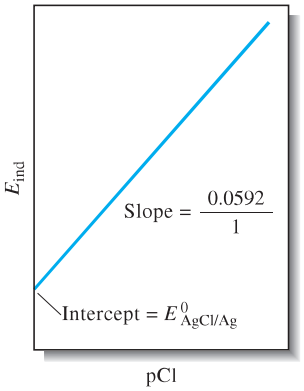


Figure 21-6 A plot of Equation 21-4 for an electrode of the second kind for Cl^-.

Inert Metallic Electrodes for Redox Systems

As noted in Chapter 18, several relatively inert conductors respond to redox systems. Such materials as platinum, gold, palladium, and carbon can be used to monitor redox systems. For example, the potential of a platinum electrode immersed in a solution containing cerium(III) and cerium(IV) is

$$E_{\text{ind}} = E^0_{Ce^{4+}/Ce^{3+}} - 0.0592 \log \frac{a_{Ce^{3+}}}{a_{Ce^{4+}}}$$

A platinum electrode is a convenient indicator electrode for titrations involving standard cerium(IV) solutions.

21D-2 Membrane Indicator Electrodes[2]

For nearly a century, the most convenient method for determining pH has involved measurement of the potential that appears across a thin glass membrane that separates two solutions with different hydrogen ion concentrations. The phenomenon on which the measurement is based was first reported in 1906 and by now has been extensively studied by many investigators. As a result, the sensitivity and selectivity of glass membranes toward hydrogen ions are reasonably well understood. Furthermore, this understanding has led to the development of other types of membranes that respond selectively to many other ions.

Membrane electrodes are sometimes called **p-ion electrodes** because the data obtained from them are usually presented as p-functions, such as pH, pCa, or pNO_3. In this section, we consider several types of p-ion membranes.

It is important to note at the outset of this discussion that membrane electrodes are fundamentally different from metal electrodes both in design and in principle. We shall use the glass electrode for pH measurements to illustrate these differences.

21D-3 The Glass Electrode for Measuring pH

Figure 21-7a shows a typical *cell* for measuring pH. The cell consists of a glass indicator electrode and a saturated calomel reference electrode immersed in the solution of unknown pH. The indicator electrode consists of a thin pH-sensitive glass membrane sealed onto one end of a heavy-walled glass or plastic tube. A small volume of dilute hydrochloric acid saturated with silver chloride is contained in the tube. The inner solution in some electrodes is a buffer containing chloride ion. A silver wire in this solution forms a silver/silver chloride reference electrode, which is connected to one of the terminals of a potential-measuring device. The calomel electrode is connected to the other terminal.

The membrane of a typical glass electrode (with a thickness of 0.03 to 0.1 mm) has an electrical resistance of 50 to 500 MΩ.

Figure 21-7a and the representation of this cell in **Figure 21-8** show that a glass-electrode system contains two reference electrodes: the external calomel electrode and the internal silver/silver chloride electrode. While the internal reference electrode is a part of the glass electrode, it is not the pH-sensing element. *It is the thin glass membrane bulb at the tip of the electrode that responds to pH.* At first, it may seem unusual that an insulator like glass (see margin note) can be used to detect ions, but keep in mind that whenever there is a charge imbalance across any material, there is an

[2]Some suggested sources for additional information on this topic are R. S. Hutchins and L. G. Bachas, in *Handbook of Instrumental Techniques for Analytical Chemistry,* F. A. Settle, ed., Upper Saddle River, NJ: Prentice-Hall, 1997; A. Evans, *Potentiometry and Ion-Selective Electrodes*, New York: Wiley, 1987; J. Koryta, *Ions, Electrodes, and Membranes*, 2nd ed., New York: Wiley, 1991.

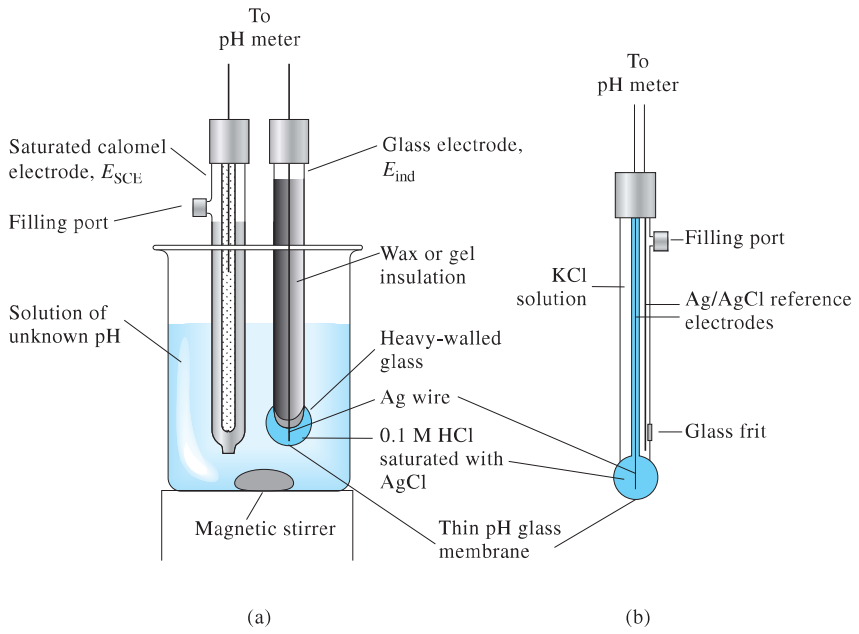


Figure 21-7 Typical electrode system for measuring pH. (a) Glass electrode (indicator) and SCE (reference) immersed in a solution of unknown pH. (b) Combination probe consisting of both an indicator glass electrode and a silver/silver chloride reference. A second silver/silver chloride electrode serves as the internal reference for the glass electrode. The two electrodes are arranged concentrically with the internal reference in the center and the external reference outside. The reference makes contact with the analyte solution through the glass frit or other suitable porous medium. Combination probes are the most common configuration of glass electrode and reference for measuring pH.

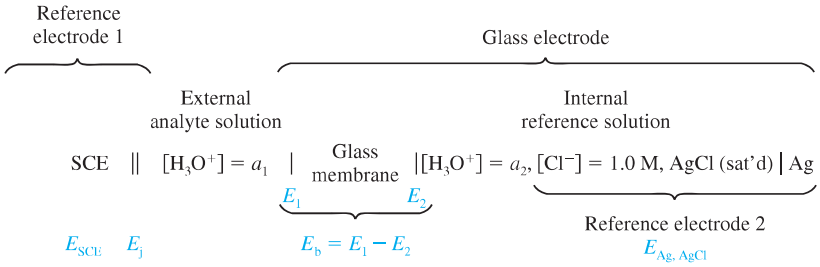


Figure 21-8 Diagram of glass/calomel cell for the measurement of pH. E_{SCE} is the potential of the reference electrode, E_j is the junction potential, a_1 is the activity of hydronium ions in the analyte solution, E_1 and E_2 are the potentials on either side of the glass membrane, E_b is the boundary potential, and a_2 is the activity of hydronium ion in the internal reference solution.

electrical potential difference across the material. In the case of the glass electrode, the concentration (and the activity) of protons inside the membrane is constant. The concentration outside the membrane is determined by the activity of hydrogen ions in the analyte solution. This concentration difference produces the potential difference that we measure with a pH meter. Notice that the internal and external reference electrodes are just the means of making electrical contact with the two sides of the glass membrane and that their potentials are essentially constant except for the junction potential, which depends to a small extent on the composition of the analyte solution. The potentials of the two reference electrodes depend on the electrochemical characteristics of their respective redox couples, but the potential across the glass membrane depends on the physicochemical characteristics of the glass and its response to ionic concentrations on both sides of the membrane. To understand how the glass electrode works, we must explore the mechanism of the creation of the charge differential across the membrane that produces the membrane potential. In the next few sections, we investigate this mechanism and the important characteristics of these membranes.

In Figure 21-7b, we see the most common configuration for measuring pH with a glass electrode. In this arrangement, the glass electrode and its Ag/AgCl internal reference electrode are positioned in the center of a cylindrical probe. Surrounding the glass electrode is the external reference electrode, which is most often of the Ag/AgCl type. The presence of the external reference electrode is not as obvious as in the dual-probe arrangement of Figure 21-7a, but the single-probe, or combination, variety is

much more convenient and can be made much smaller than the dual system. The pH-sensitive glass membrane is attached to the tip of the electrode. These glass pH electrodes are manufactured in many different physical shapes and sizes (5 cm to 5 μm) to suit a broad range of laboratory and industrial applications.

The Composition and Structure of Glass Membranes

Much research has been devoted to the effects of glass composition on the sensitivity of membranes to protons and other cations, and a number of formulations are now used for the manufacture of electrodes. Corning 015 glass, which has been widely used for membranes, consists of approximately 22% Na_2O, 6% CaO, and 72% SiO_2. Membranes made from this glass exhibit excellent specificity to hydrogen ions up to a pH of about 9. At higher pH values, however, the glass becomes somewhat responsive to sodium as well as to other singly charged cations. Other glass formulations are now in use in which sodium and calcium ions are replaced to various degree by barium and lithium ions. These membranes have superior selectivity and lifetime.

As shown in **Figure 21-9**, a silicate glass used for membranes consists of an infinite three-dimensional network of groups in which each silicon atom is bonded to four oxygen atoms and each oxygen atom is shared by two silicon atoms. Within the empty spaces (interstices) inside this structure are enough cations to balance the negative charge of the silicate groups. Singly charged cations, such as sodium and lithium, can move around in the lattice and are responsible for electrical conduction within the membrane.

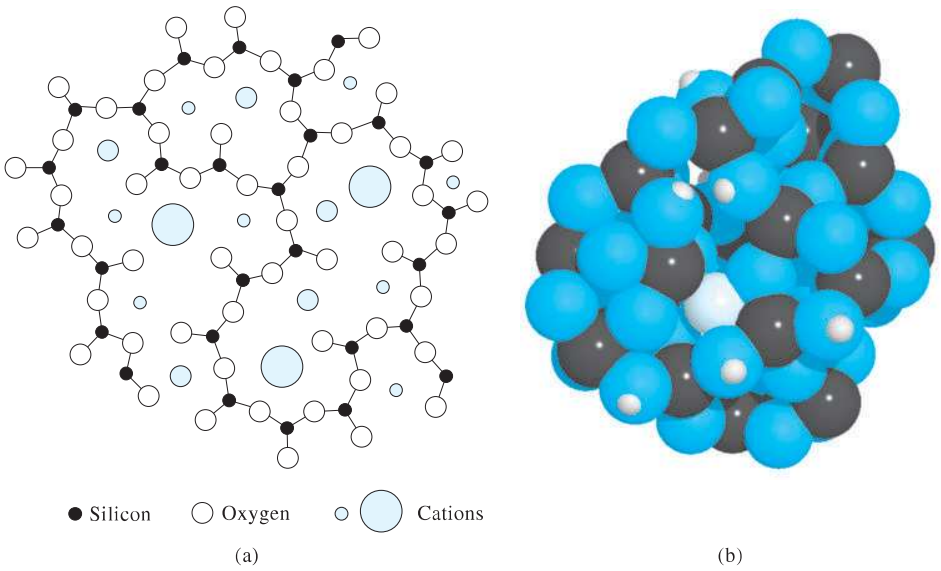


Figure 21-9 (a) Cross-sectional view of a silicate glass structure. In addition to the three Si—O bond shown, each silicon is bonded to an additional oxygen atom, either above or below the plane of the paper. (Reprinted (adapted) with permission from G. A. Perley, *Anal. Chem.*, **1949**, *21*, 395, **DOI**: 10.1021/ac60027a013. Copyright 1949 American Chemical Society.) (b) Model showing three-dimensional structure of amorphous silica with Na^+ ion (large dark green) and several H^+ ions (small dark green) incorporated. Note that the Na^+ ion is surrounded by a cage of oxygen atoms and that each proton in the amorphous lattice is attached to an oxygen. The cavities in the structure, the small size, and the high mobility of the proton ensure that protons can migrate deep into the surface of the silica. Other cations and water molecules may be incorporated into the interstices of the structure as well.

The two surfaces of a glass membrane must be hydrated before it will function as a pH electrode. Nonhygroscopic glasses show no pH function. Even hygroscopic glasses lose their pH sensitivity after dehydration by storage over a desiccant. The effect is reversible, however, and the response of a glass electrode can be restored by soaking it in water.

Glasses that absorb water are said to be **hygroscopic**.

The hydration of a pH-sensitive glass membrane involves an ion-exchange reaction between singly charged cations in the interstices of the glass lattice and hydrogen ions from the solution. The process involves +1 cations exclusively because +2 and +3 cations are too strongly held within the silicate structure to exchange with ions in the solution. The ion-exchange reaction can then be written as

$$\underset{\text{soln}}{H^+} + \underset{\text{glass}}{Na^+Gl^-} \rightleftharpoons \underset{\text{soln}}{Na^+} + \underset{\text{glass}}{H^+Gl^-} \qquad (21\text{-}5)$$

Oxygen atoms attached to only one silicon atom are the negatively charged Gl^- sites shown in this equation. The equilibrium constant for this process is so large that the surfaces of a hydrated glass membrane normally consist entirely of silicic acid (H^+Gl^-). There is an exception to this situation in highly alkaline media, where the hydrogen ion concentration is extremely small and the sodium ion concentration is large. Under this condition, a significant fraction of the sites are occupied by sodium ions.

Membrane Potentials

The lower part of Figure 21-8 shows four potentials that develop in a cell when pH is being determined with a glass electrode. Two of these potentials, $E_{Ag,AgCl}$ and E_{SCE}, are reference electrode potentials that are constant. There is a third potential, the junction potential, E_j, across the salt bridge that separates the calomel electrode from the analyte solution. This junction and its associated potential are found in all cells used to make potentiometric measurements of ion concentration. The fourth, and most important, potential shown in Figure 21-8 is the **boundary potential**, E_b, *which varies with the pH of the analyte solution*. The two reference electrodes simply provide electrical contacts with the solutions so that changes in the boundary potential can be measured.

The Boundary Potential

Figure 21-8 shows that the boundary potential is determined by potentials, E_1 and E_2, which appear at the two *surfaces* of the glass membrane. The source of these two potentials is the charge that accumulates as a consequence of the reactions

$$\underset{\text{glass}_1}{H^+Gl^-(s)} \rightleftharpoons \underset{\text{soln}_1}{H^+(aq)} + \underset{\text{glass}_1}{Gl^-(s)} \qquad (21\text{-}6)$$

$$\underset{\text{glass}_2}{H^+Gl^-(s)} \rightleftharpoons \underset{\text{soln}_2}{H^+(aq)} + \underset{\text{glass}_2}{Gl^-(s)} \qquad (21\text{-}7)$$

where subscript 1 refers to the interface between the exterior of the glass and the analyte solution and subscript 2 refers to the interface between the internal solution and the interior of the glass. These two reactions cause the two glass surfaces to be negatively charged with respect to the solutions with which they are in contact. These negative charges at the surfaces produce the two potentials E_1 and E_2 shown in Figure 21-8. The hydrogen ion concentrations in the solutions on the two sides of the membrane control the positions of the equilibria of Equations 21-7 and 21-8 that in turn determine E_1 and E_2. When the positions of the two equilibria differ, the surface where the greater dissociation has occurred is negative with respect to the

other surface. The resulting difference in potential between the two surfaces of the glass is the boundary potential, which is related to the activities of hydrogen ions in each of the solutions by the Nernst-like equation

$$E_b = E_1 - E_2 = 0.0592 \log \frac{a_1}{a_2} \tag{21-8}$$

where a_1 is the activity of the analyte solution and a_2 is that of the internal solution. For a glass pH electrode, the hydrogen ion activity of the internal solution, a_2, is held constant so that Equation 21-8 simplifies to

$$E_b = L' + 0.0592 \log a_1 = L' - 0.0592 \text{ pH} \tag{21-9}$$

where

$$L' = -0.0592 \log a_2$$

The boundary potential is then a measure of the hydrogen ion activity (pH) of the external solution.

The significance of the potentials and the potential differences shown in Equation 21-8 is illustrated by the potential profiles shown in **Figure 21-10**. The profiles are plotted across the membrane from the analyte solution on the left

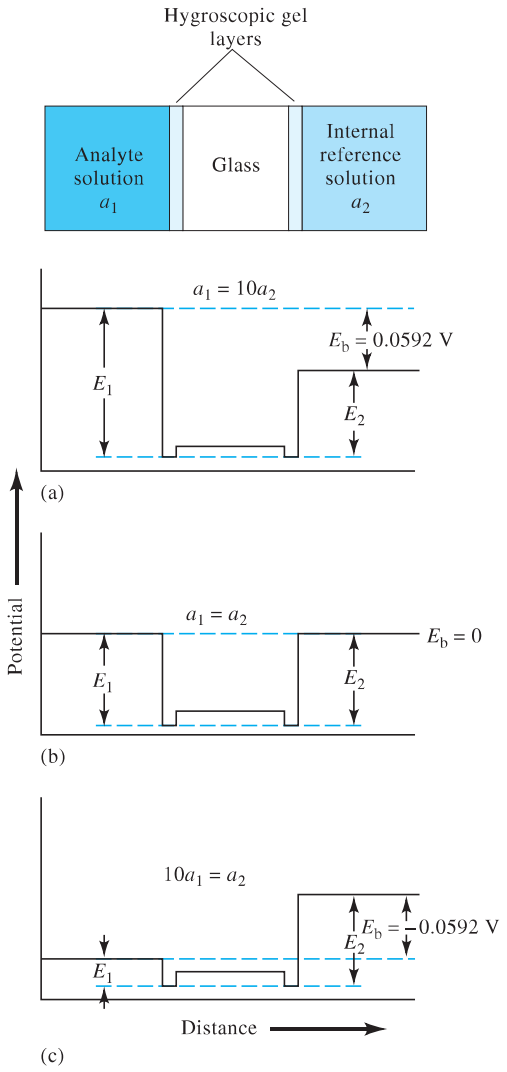


Figure 21-10 Potential profile across a glass membrane from the analyte solution to the internal reference solution. The reference electrode potentials are not shown.

through the membrane to the internal solution on the right. The important thing to note about these profiles is that regardless of the absolute potential inside the hygroscopic layers or the glass, the boundary potential is determined by the *difference* in potential on either side of the glass membrane that is in turn determined by the proton activity on each side of the membrane.

The Asymmetry Potential

When identical solutions and reference electrodes are placed on the two sides of a glass membrane, the boundary potential should in principle be zero. Frequently, however, we find a small asymmetry potential that changes gradually with time.

The sources of the asymmetry potential are obscure but undoubtedly include such causes as differences in strain on the two surfaces of the membrane created during manufacture, mechanical abrasion on the outer surface during use, and chemical etching of the outer surface. To eliminate the bias caused by the asymmetry potential, all membrane electrodes must be calibrated against one or more standard analyte solutions. Calibrations should be carried out at least daily and more often when the electrode is heavily used.

The Glass Electrode Potential

The potential of a glass indicator electrode, E_{ind}, has three components: (1) the boundary potential, given by Equation 21-8; (2) the potential of the internal Ag/AgCl reference electrode; and (3) the small asymmetry potential, E_{asy}, which changes slowly with time. In equation form, we may write

$$E_{ind} = E_b + E_{Ag/AgCl} + E_{asy}$$

Substitution of Equation 21-9 for E_b gives

$$E_{ind} = L' + 0.0592 \log a_1 + E_{Ag/AgCl} + E_{asy}$$

or

$$E_{ind} = L + 0.0592 \log a_1 = L - 0.0592\ \text{pH} \qquad (21\text{-}10)$$

where L is a combination of the three constant terms. Compare Equations 21-10 and 21-3. Although these two equations are similar in form and both potentials are produced by separation of charge, remember that *the mechanisms of charge separation that result in these expressions are considerably different.*

The Alkaline Error

In basic solutions, glass electrodes respond to the concentration of both hydrogen ion and alkali metal ions. The magnitude of the resulting alkaline error for four different glass membranes is shown in **Figure 21-11** (curves *C* to *F*). These curves refer to solutions in which the sodium ion concentration was held constant at 1 M while the pH was varied. Note that the error ($pH_{read} - pH_{true}$) is negative (that is, the measured pH values are lower than the true values), suggesting that the electrode is responding to sodium ions as well as to protons. This observation is confirmed by data obtained for solutions containing different sodium ion concentrations. Thus, at pH 12, the electrode with a Corning 015 membrane (curve *C* in Figure 21-11) registered a pH of 11.3 when immersed in a solution having a sodium ion concentration of 1 M but 11.7 in a solution that was 0.1 M in this ion. All singly charged cations induce an alkaline error whose magnitude depends on both the cation in question and the composition of the glass membrane.

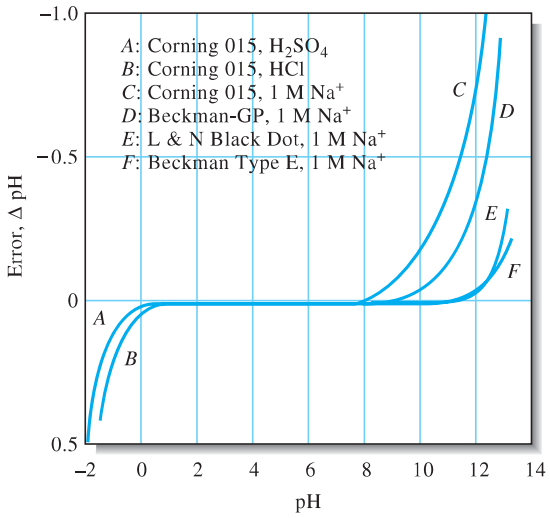


Figure 21-11 Acid and alkaline errors for selected glass electrodes at 25°C. (R.G. Bates, *Determination of pH*, 2nd ed., p.265. New York: Wiley, 1973. Reprinted by permission of the author's estate.)

The alkaline error can be satisfactorily explained by assuming an exchange equilibrium between the hydrogen ions on the glass surface and the cations in solution. This process is simply the reverse of that shown in Equation 21-5:

$$\underset{\text{glass}}{H^+Gl^-} + \underset{\text{soln}}{B^+} \rightleftharpoons \underset{\text{glass}}{B^+Gl^-} + \underset{\text{soln}}{H^+}$$

where B^+ represents some singly charged cation, such as sodium ion.

The equilibrium constant for this reaction is

In Equation 21-11, b_1 represents the activity of some singly charged cation such as Na^+ or K^+.

$$K_{ex} = \frac{a_1 b_1'}{a_1' b_1} \tag{21-11}$$

where a_1 and b_1 represent the activities of H^+ and B^+ in solution and a_1' and b_1' are the activities of these ions on the glass surface. Equation 21-11 can be rearranged to give ratio of the activities B^+ to H^+ on the glass surface:

$$\frac{b_1'}{a_1'} = K_{ex}\frac{b_1}{a_1}$$

For the glasses used for pH electrodes, K_{ex} is typically so small that the activity ratio b_1'/a_1' is minuscule. The situation differs in strongly alkaline media, however. For example, b_1'/a_1' for an electrode immersed in a pH 11 solution that is 1 M in sodium ions (see Figure 21-11) is $10^{11} \times K_{ex}$. Under these conditions, the activity of the sodium ions relative to that of the hydrogen ions becomes so large that the electrode responds to both species.

Describing Selectivity

The effect of an alkali metal ion on the potential across a membrane can be accounted for by inserting an additional term in Equation 21-9 to give

$$E_b = L' + 0.0592 \log (a_1 + k_{H,B} b_1) \tag{21-12}$$

The **selectivity coefficient** is a measure of the response of an ion-selective electrode to other ions.

where $k_{H,B}$ is the **selectivity coefficient** for the electrode. Equation 21-12 applies not only to glass indicator electrodes for hydrogen ion but also to all other types

of membrane electrodes. Selectivity coefficients range from zero (no interference) to values greater than unity. Thus, if an electrode for ion A responds 20 times more strongly to ion B than to ion A, $k_{H,B}$ has a value of 20. If the response of the electrode to ion C is 0.001 of its response to A (a much more desirable situation), $k_{H,B}$ is 0.001.[3]

The product $k_{H,B}b_1$ for a glass pH electrode is usually small relative to a_1 provided that the pH is less than 9; under these conditions, Equation 21-12 simplifies to Equation 21-9. At high pH values and at high concentrations of a singly charged ion, however, the second term in Equation 21-12 assumes a more important role in determining E_b, and an alkaline error is encountered. For electrodes specifically designed for work in highly alkaline media (curve *E* in Figure 21-11), the magnitude of $k_{H,B}b_1$ is appreciably smaller than for ordinary glass electrodes.

The Acid Error

As shown in Figure 21-11, the typical glass electrode exhibits an error, opposite in sign to the alkaline error, in solution of pH less than about 0.5. The negative error ($pH_{read} - pH_{true}$) indicates that pH readings tend to be too high in this region. The magnitude of the error depends on a variety of factors and is generally not very reproducible. All the causes of the acid error are not well understood, but one source is a saturation effect that occurs when all the surface sites on the glass are occupied with H^+ ions. Under these conditions, the electrode no longer responds to further increases in the H^+ concentration, and the pH readings are too high.

21D-4 Glass Electrodes for Other Cations

The alkaline error in early glass electrodes led to investigations concerning the effect of glass composition on the magnitude of this error. One consequence has been the development of glasses for which the alkaline error is negligible below about pH 12 (see curves *E* and *F*, Figure 21-11). Other studies have discovered glass compositions that permit the determination of cations other than hydrogen. Incorporation of Al_2O_3 or B_2O_3 in the glass has the desired effect. Glass electrodes that permit the direct potentiometric measurement of such singly charged species as Na^+, K^+, NH_4^+, Rb^+, Cs^+, Li^+, and Ag^+ have been developed. Some of these glasses are reasonably selective toward particular singly charged cations. Glass electrodes for Na^+, Li^+, NH_4^+, and total concentration of univalent cations are now available from commercial sources.

21D-5 Liquid-Membrane Electrodes

The potential of liquid-membrane electrodes develops across the interface between the solution containing the analyte and a liquid-ion exchanger that selectively bonds with the analyte ion. These electrodes have been developed for the direct potentiometric measurement of numerous polyvalent cations as well as certain anions.

Figure 21-12 is a schematic of a liquid-membrane electrode for calcium. It consists of a conducting membrane that selectively binds calcium ions, an internal solution containing a fixed concentration of calcium chloride, and a silver electrode that is coated with silver chloride to form an internal reference electrode. Notice the similarities between the liquid-membrane electrode and the glass electrode, as shown in

[3]For tables of selectivity coefficients for a variety of membranes and ionic species, see Y. Umezawa, *CRC Handbook of Ion Selective Electrodes: Selectivity Coefficients*, Boca Raton, FL: CRC Press, 1990.

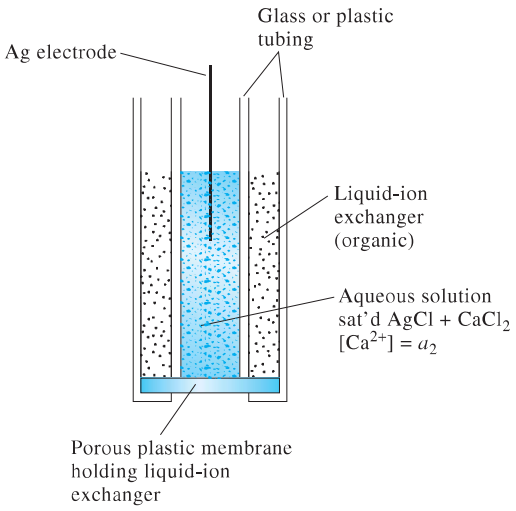


Figure 21-12 Diagram of a liquid-membrane electrode for Ca^{2+}.

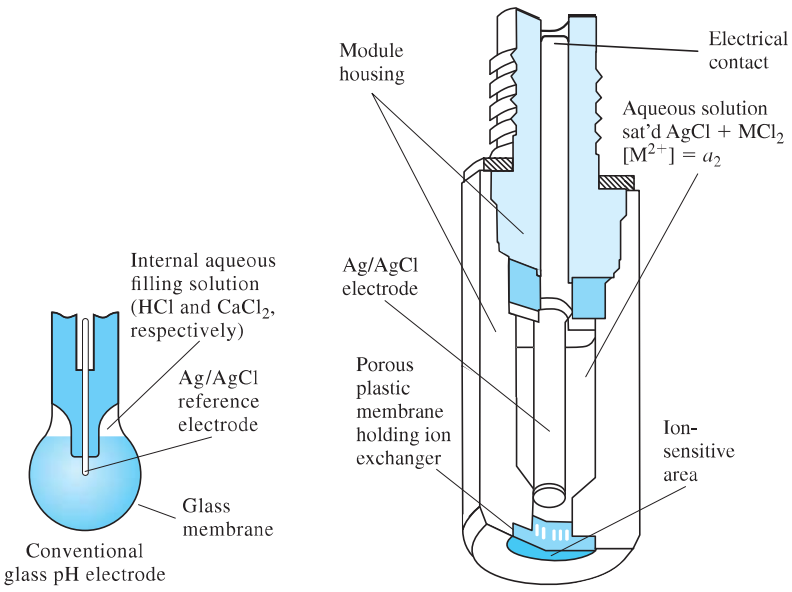


Figure 21-13 Comparison of a liquid-membrane calcium ion electrode with a glass pH electrode. (Courtesy of Thermo Orion, Beverly, MA.)

Figure 21-13. The active membrane ingredient is an ion exchanger that consists of a calcium dialkyl phosphate that is nearly insoluble in water. In the electrode shown in Figures 21-12 and 21-13, the ion exchanger is dissolved in an immiscible organic liquid that is forced by gravity into the pores of a hydrophobic porous disk. This disk then serves as the membrane that separates the internal solution from the analyte solution. In a more recent design, the ion exchanger is immobilized in a tough polyvinyl chloride gel attached to the end of a tube that holds the internal solution and reference electrode (see Figure 21-13, right). In either design, a dissociation equilibrium develops at each membrane interface that is analogous to Equations 21-6 and 21-7:

Hydrophobia means fear of water. The hydrophobic disk is porous toward organic liquids but repels water.

$$\underset{\text{organic}}{[(RO)_2POO]_2Ca} \rightleftharpoons \underset{\text{organic}}{2(RO)_2POO^-} + \underset{\text{aqueous}}{Ca^{2+}}$$

where R is a high-molecular-mass aliphatic group. As with the glass electrode, a potential develops across the membrane when the extent of dissociation of the ion exchanger dissociation at one surface differs from that at the other surface.

This potential is a result of differences in the calcium ion activity of the internal and external solutions. The relationship between the membrane potential and the calcium ion activities is given by an equation that is similar to Equation 21-8:

$$E_b = E_1 - E_2 = \frac{0.0592}{2} \log \frac{a_1}{a_2} \qquad (21\text{-}13)$$

where a_1 and a_2 are the activities of calcium ion in the external analyte and internal standard solutions, respectively. Since the calcium ion activity of the internal solution is constant,

$$E_b = N + \frac{0.0592}{2} \log a_1 = N - \frac{0.0592}{2} \text{pCa} \qquad (21\text{-}14)$$

where N is a constant (compare Equations 21-14 and 21-9). Note that, because calcium is divalent, the value of n in the denominator of the coefficient of the logarithmic term is 2.

The sensitivity of the liquid-membrane electrode for calcium ion is reported to be 50 times greater than for magnesium ion and 1000 times greater than for sodium or potassium ions. Calcium ion activities as low as 5×10^{-7} M can be measured. Performance of the electrode is independent of pH in the range between 5.5 and 11. At lower pH levels, hydrogen ions undoubtedly replace some of the calcium ions on the exchanger; the electrode then becomes sensitive to pH as well as to pCa.

The calcium ion liquid-membrane electrode is a valuable tool for physiological investigations because this ion plays important roles in such processes as nerve conduction, bone formation, muscle contraction, cardiac expansion and contraction, renal tubular function, and perhaps hypertension. Most of these processes are more influenced by the activity than the concentration of the calcium ion; activity, of course, is the parameter measured by the membrane electrode. Therefore, the calcium ion electrode as well as the potassium ion electrode and others are important tools in studying physiological processes.

A liquid-membrane electrode specific for potassium ion is also of great value for physiologists because the transport of neural signals appears to involve movement of this ion across nerve membranes. Investigation of this process requires an electrode that can detect small concentrations of potassium ion in media that contain much larger concentrations of sodium ion. Several liquid-membrane electrodes show promise in meeting this requirement. One is based on the antibiotic valinomycin, a cyclic ether that has a strong affinity for potassium ion. Of equal importance is the observation that a liquid membrane consisting of valinomycin in diphenyl ether is about 10^4 times as responsive to potassium ion as to sodium ion.[4] **Figure 21-14** is a photomicrograph of a tiny electrode used for determining the potassium content of a single cell.

Table 21-2 lists some liquid-membrane electrodes available from commercial sources. The anion-sensitive electrodes listed make use of a solution containing an anion-exchange resin in an organic solvent. Liquid-membrane electrodes in which the exchange liquid is held in a polyvinyl chloride gel have been developed for Ca^{2+}, K^+, NO_3^-, and BF_4^-. These have the appearance of crystalline electrodes, which are considered in the following section. A homemade liquid-membrane ion-selective electrode is described in Feature 21-1.

Ion-selective microelectrodes can be used to make measurements of ion activities within a living organism.

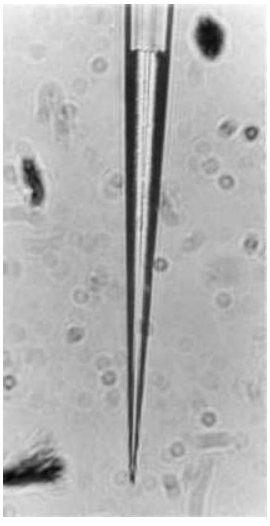


Figure 21-14 Photograph of a potassium liquid ion exchanger microelectrode with 125 μm of ion exchanger inside the tip. The magnification of the original photo was 400×. (Reprinted with permission from *Anal. Chem.*, March **1971**, *43*(3), 89A-93A. Copyright 1971 American Chemical Society.)

[4] M. S. Frant and J. W. Ross, Jr., *Science*, **1970**, *167*, 987, **DOI**: 10.1126/science.167.3920.987.

TABLE 21-2

Characteristics of Liquid-Membrane Electrodes*

Analyte Ion	Concentration Range, M†	Major Interferences‡
NH_4^+	10^0 to 5×10^{-7}	<1 H^+, 5×10^{-1} Li^+, 8×10^{-2}, Na^+, 6×10^{-4} K^+, 5×10^{-2} Cs^+, >1 Mg^{2+}, >1 Ca^{2+}, >1 Sr^{2+}, >0.5 Sr^{2+}, 1×10^{-2} Zn^{2+}
Cd^{2+}	10^0 to 5×10^{-7}	Hg^{2+} and Ag^+ (poisons electrode at $>10^{-7}$ M), Fe^{3+} (at $>0.1[Cd^{2+}]$, Pb^{2+} (at $>[Cd^{2+}]$), Cu^{2+} (possible)
Ca^{2+}	10^0 to 5×10^{-7}	10^{-5} Pb^{2+}; 4×10^{-3} Hg^{2+}, H^+, 6×10^{-3} Sr^{2+}; 2×10^{-2} Fe^{2+}; 4×10^{-2} Cu^{2+}; 5×10^{-2} Ni^{2+}; 0.2 NH_3; 0.2 Na^+; 0.3 $Tris^+$; 0.3 Li^+; 0.4 K^+; 0.7 Ba^{2+}; 1.0 Zn^{2+}; 1.0 Mg^{2+}
Cl^-	10^0 to 5×10^{-6}	Maximum allowable ratio of interferent to $[Cl^-]$: OH^- 80, Br^- 3×10^{-3}; I^- 5×10^{-7}, S^{2-} 10^{-6}, CN^- 2×10^{-7}, NH_3 0.12, $S_2O_3^{2-}$ 0.01
BF_4^-	10^0 to 7×10^{-6}	5×10^{-7} ClO_4^-; 5×10^{-6} I^-; 5×10^{-5} ClO_3^-; 5×10^{-4} CN^-; 10^{-3} Br^-; 10^{-3} NO_2^-; 5×10^{-3} NO_3^-; $3 \times 10^{-3}HCO_3^-$, 5×10^{-2} Cl^-; 8×10^{-2} $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}; 0.2 OAc^-; 0.6 F^-; 1.0 SO_4^{2-}
NO_3^-	10^0 to 7×10^{-6}	$10^{-7}ClO_4^-$; 5×10^{-6}; I^-; 5×10^{-5} ClO_3^-; 10^{-4} CN^-; 7×10^{-4} Br^-; 10^{-3} HS^-; 10^{-2} HCO_3^-, 2×10^{-2} CO_3^{2-}; 3×10^{-2} Cl^-; 5×10^{-2} $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}; 0.2 OAc^-; 0.6 F^-; 1.0 SO_4^{2-}
NO_2^-	1.4×10^{-6} to 3.6×10^{-6}	7×10^{-1} salicylate, 2×10^{-3} I^-, 10^{-1} Br^-, 3×10^{-1} ClO_3^-, 2×10^{-1} acetate, 2×10^{-1} HCO_3^-, 2×10^{-1} NO_3^-, 2×10^{-1} SO_4^{2-}, 1×10^{-1} Cl^-, 1×10^{-1} ClO_4^-, 1×10^{-1} F^-
ClO_4^-	10^0 to 7×10^{-6}	2×10^{-3} I^-; 2×10^{-2} ClO_3^-; 4×10^{-2} CN^-, Br^-; 5×10^{-2} NO_2^-, NO_3^-; 2 HCO_3^-, CO_3^{2-}; Cl^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, OAc^-, F^-, SO_4^{2-}
K^+	10^0 to 1×10^{-6}	3×10^{-4} Cs^+; 6×10^{-3} NH_4^+, Tl^+; 10^{-2} H^+; 1.0 Ag^+, $Tris^+$; 2.0 Li^+, Na^+
Water hardness ($Ca^{2+}+Mg^{2+}$)	10^{-3} to 6×10^{-6}	3×10^{-5} Cu^{2+}, Zn^{2+}; 10^{-4} Ni^{2+}; 4×10^{-4} Sr^{2+}; 6×10^{-5} Fe^{2+}; 6×10^{-4} Ba^{2+}; 3×10^{-2} Na^+; 0.1 K^+

All electrodes are the plastic-membrane type. All values are selectivity coefficients unless otherwise noted.
†From product catalog, Boston, MA: Thermo Orion, 2006.
‡From product instruction manuals, Boston, MA: Thermo Orion, 2003.

FEATURE 21-1

An Easily Constructed Liquid-Membrane Ion-Selective Electrode

You can make a liquid-membrane ion-selective electrode with glassware and chemicals available in most laboratories.[5] All you need are a pH meter, a pair of reference electrodes, a fritted-glass filter crucible or tube, trimethylchlorosilane, and a liquid ion exchanger.

First, cut the filter crucible (or alternatively, a fritted tube), as shown in Figure 21F-1. Carefully clean and dry the crucible and then draw a small amount of trimethylchlorosilane into the frit. This coating makes the glass in the frit hydrophobic. Rinse the frit with water, dry, and apply a commercial liquid ion exchanger to it. After a minute, remove the excess exchanger. Add a few milliliters of a 10^{-2} M solution of the ion of interest to the crucible, insert a reference electrode into the solution, and voilá, you have a very nice ion-selective electrode. The exact details of washing, drying, and preparing the electrode are provided in the original article.

Connect the ion-selective electrode and the second reference electrode to the pH meter, as shown in Figure 21F-1. Prepare a series of standard solutions of the ion of interest, measure the cell potential for each concentration, plot a working curve of

[5]See T. K. Christopoulus and E. P. Diamandis, *J. Chem. Educ.*, **1988**, *65*, 648, **DOI**: 10.1021/ed065p648.

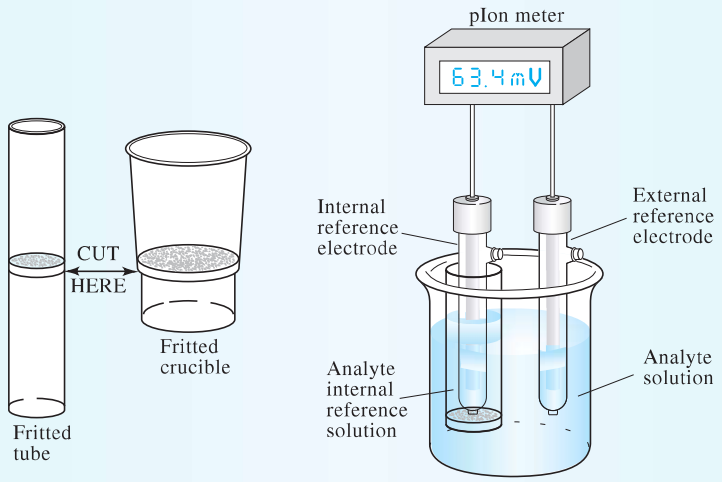


Figure 21F-1 A homemade liquid-membrane electrode.

E_{cell} versus log c, and perform a least-squares analysis on the data (see Chapter 8). Compare the slope of the line with the theoretical slope of (0.0592 V)/n. Measure the potential for an unknown solution of the ion and calculate the concentration from the least-squares parameters.

21D-6 Crystalline-Membrane Electrodes

Considerable work has been devoted to the development of solid membranes that are selective toward anions in the same way that some glasses respond to cations. We have seen that anionic sites on a glass surface account for the selectivity of a membrane toward certain cations. By analogy, a membrane with cationic sites might be expected to respond selectively toward anions.

Membranes prepared from cast pellets of silver halides have been used successfully in electrodes for the selective determination of chloride, bromide, and iodide ions. In addition, an electrode based on a polycrystalline Ag_2S membrane is offered by one manufacturer for the determination of sulfide ion. In both types of membranes, silver ions are sufficiently mobile to conduct electricity through the solid medium. Mixtures of PbS, CdS, and CuS with Ag_2S provide membranes that are selective for Pb^{2+}, Cd^{2+}, and Cu^{2+}, respectively. Silver ion must be present in these membranes to conduct electricity because divalent ions are immobile in crystals. The potential that develops across crystalline solid-state electrodes is described by a relationship similar to Equation 21-9.

A crystalline electrode for fluoride ion is available from commercial sources. The membrane consists of a slice of a single crystal of lanthanum fluoride that has been doped with europium(II) fluoride to improve its conductivity. The membrane, supported between a reference solution and the solution to be measured, shows a theoretical response to changes in fluoride ion activity from 10^0 to 10^{-6} M. The electrode is selective for fluoride ion over other common anions by several orders of magnitude; only hydroxide ion appears to offer serious interference.

Some solid-state electrodes available from commercial sources are listed in **Table 21-3**.

TABLE 21-3

Characteristics of Solid-State Crystalline Electrodes*

Analyte Ion	Concentration Range, M	Major Interferences
Br^-	10^0 to 5×10^{-6}	CN^-, I^-, S^{2-}
Cd^{2+}	10^{-1} to 1×10^{-7}	Fe^{2+}, Pb^{2+}, Hg^{2+}, Ag^+, Cu^{2+}
Cl^-	10^0 to 5×10^{-5}	CN^-, I^-, Br^-, S^{2-}, OH^-, NH_3
Cu^{2+}	10^{-1} to 1×10^{-8}	Hg^{2+}, Ag^+, Cd^{2+}
CN^-	10^{-2} to 1×10^{-6}	S^{2-}, I^-
F^-	Sat'd to 1×10^{-6}	OH^-
I^-	10^0 to 5×10^{-8}	CN^-
Pb^{2+}	10^{-1} to 1×10^{-6}	Hg^{2+}, Ag^+, Cu^{2+}
Ag^+/S^{2-}	Ag^+: 10^0 to 1×10^{-7} S^{2-}: 10^0 to 1×10^{-7}	Hg^{2+}
SCN^-	10^0 to 5×10^{-6}	I^-, Br^-, CN^-, S^{2-}

*From *Orion Guide to Ion Analysis,* Boston, MA: Thermo Orion, 1992.

21D-7 Ion-Sensitive Field Effect Transistors (ISFETs)

The **field effect transistor**, or the **metal oxide field effect transistor (MOSFET)**, is a tiny solid-state semiconductor device that is widely used in computers and other electronic circuits as a switch to control current flow in circuits. One of the problems in using this type of device in electronic circuits has been its pronounced sensitivity to ionic surface impurities, and a great deal of money and effort has been expended by the electronic industry in minimizing or eliminating this sensitivity in order to produce stable transistors.

Scientists have exploited the sensitivities of MOSFETs to surface ionic impurities for the selective potentiometric determination of various ions. These studies have led to the development of a number of different **ion-sensitive field effect transistors** termed **ISFETs**. The theory of their selective ion sensitivity is well understood and is described in Feature 21-2.[6]

ISFETs stands for ion-sensitive field effect transistors.

ISFETs offer a number of significant advantages over membrane electrodes including ruggedness, small size, inertness toward harsh environments, rapid response, and low electrical impedance. In contrast to membrane electrodes,

FEATURE 21-2

The Structure and Performance of Ion-Sensitive Field Effect Transistors

The metal oxide field effect transistor (MOSFET) is a solid-state semiconductor device that is used widely for switching signals in computers and many other types of electronic circuits. **Figure 21F-2** shows a cross-sectional diagram (a) and a circuit symbol (b) for an *n*-channel enhancement mode MOSFET. Modern semiconductor fabrication techniques are used to construct the MOSFET on the surface of a piece of *p*-type semiconductor called the substrate. For a discussion of the characteristics of *p*-type and *n*-type semiconductors, refer to the paragraphs on silicon photodiodes in Section 25A-4. As shown in Figure 21F-2a, two islands of *n*-type semiconductors are formed on the surface of the *p*-type substrate, and the surface is then covered by insulating SiO_2. The last step in the fabrication process is the deposition of metallic

[6]For a detailed explanation of the theory of ISFETs, see J. Janata, *Principles of Chemical Sensors,* 2nd ed., New York: Plenum, 2009, pp. 156–167.

conductors that are used to connect the MOSFET to external circuits. There are a total of four such connections to the drain, the gate, the source, and the substrate as shown in the figure.

The area on the surface of the *p*-type material between the drain and source is called the channel (see the dark shaded area in Figure 21F-2a). Note that the channel is separated from the gate connection by an insulating layer of SiO_2. When an electrical potential is applied between the gate and the source, the electrical conductivity of the channel is enhanced by a factor that is related to the size of the applied potential.

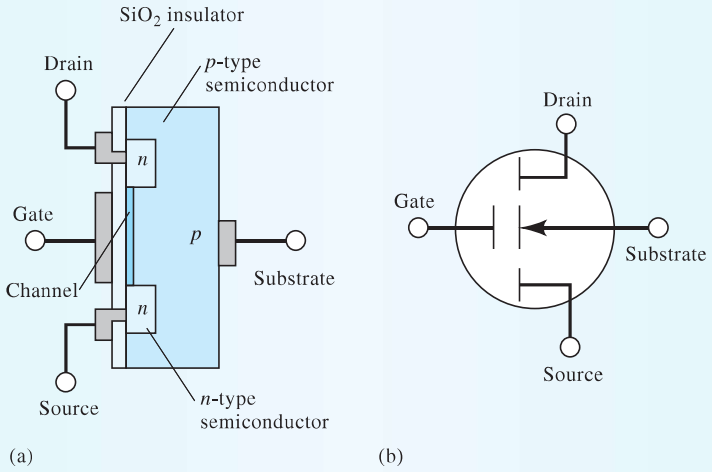


Figure 21F-2 A metal oxide field effect transistor (MOSFET). (a) Cross-sectional diagram. (b) Circuit symbol.

The **ion-sensitive field effect transistor**, or **ISFET**, is very similar in construction and function to an *n*-channel enhancement mode MOSFET. The ISFET differs only in that variation in the concentration of the ions of interest provides the variable gate voltage to control the conductivity of the channel. As shown in **Figure 21F-3**, instead of the usual metallic contact, the face of the ISFET is covered with an insulating layer of silicon nitride. The analytical solution, containing hydronium ions in this example, is in contact with this insulating layer and with a reference electrode. The surface of the gate insulator functions very much like the surface of a glass electrode. Protons from the hydronium ions in the test solution are absorbed by available microscopic sites on the silicon nitride. Any change in the hydronium ion concentration (or activity) of the solution results in a change in the concentration of adsorbed protons. The change in concentration of adsorbed protons then gives rise to a changing electrochemical potential between the gate and the source that in turn changes the conductivity of the channel of the ISFET. The conductivity of the channel can be monitored electronically to provide a signal that is proportional to the logarithm of the activity of hydronium ion in the solution. Note that the entire ISFET except the gate insulator is coated with a polymeric encapsulant to insulate all electrical connections from the analyte solution.

The ion-sensitive surface of the ISFET is naturally sensitive to pH changes, but the device may be modified so that it becomes sensitive to other species by coating the silicon nitride gate insulator with a polymer containing molecules that tend to form complexes with species other than hydronium ion. Furthermore, several ISFETs

(*continued*)

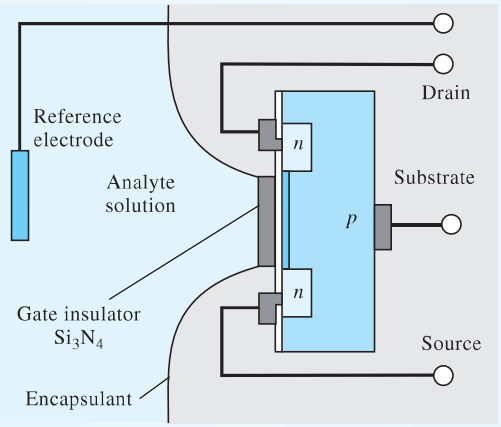


Figure 21F-3 An ion-sensitive field effect transistor (ISFET) for measuring pH.

may be fabricated on the same substrate so that multiple measurements may be made at the same time. All of the ISFETs may detect the same species to enhance accuracy and reliability, or each ISFET may be coated with a different polymer so that measurements of several different species may be made. Their small size (about 1 to 2 mm^2), rapid response time relative to glass electrodes, and ruggedness suggest that ISFETs may be the ion detectors of the future for many applications.

ISFETs do not require hydration before use and can be stored indefinitely in the dry state. Despite these many advantages, no ISFET-specific ion electrodes appeared on the market until the early 1990s, over 20 years after their invention. The reason for this delay is that manufacturers were unable to develop the technology of encapsulating the devices to give a product that did not exhibit drift and instability. Several companies now produce ISFETs for the determination of pH, but as of the writing of this text, these electrodes are certainly not as routinely used as the glass pH electrode.

21D-8 Gas-Sensing Probes

A **gas-sensing probe** is a galvanic *cell* whose potential is related to the concentration of a gas in a solution. In instrument brochures, these devices are often called gas-sensing electrodes, which is a misnomer as discussed later in this section.

Figure 21-15 illustrates the essential features of a potentiometric gas-sensing probe, which consists of a tube containing a reference electrode, a specific ion electrode, and an electrolyte solution. A thin, replaceable, gas-permeable membrane attached to one end of the tube serves as a barrier between the internal and analyte solutions. As can be seen from Figure 21-15, this device is a complete electrochemical cell and is more properly referred to as a probe rather than an electrode, a term that is frequently encountered in advertisements by instrument manufacturers. Gas-sensing probes are used widely for determining dissolved gases in water and other solvents.

Membrane Composition

A *microporous membrane* is fabricated from a hydrophobic polymer. As the name implies, the membrane is highly porous (the average pore size is less than 1 μm) and allows the free passage of gases; at the same time, the water-repellent polymer prevents

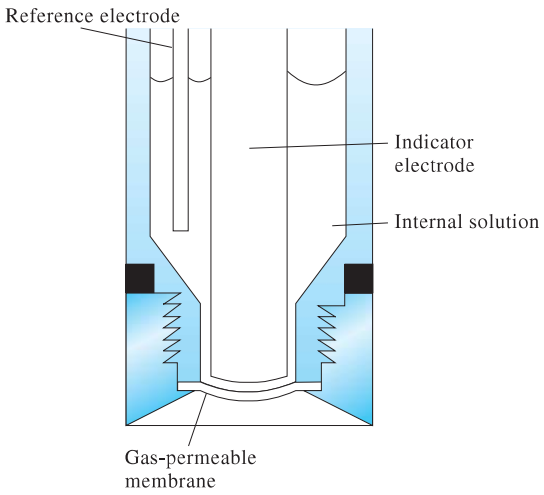


Figure 21-15 Diagram of a gas-sensing probe.

water and solute ions from entering the pores. The thickness of the membrane is about 0.1 mm.

The Mechanism of Response

Using carbon dioxide as an example, we can represent the transfer of gas to the internal solution in Figure 21-15 by the following set of equations:

$$\underset{\text{analyte solution}}{CO_2(aq)} \rightleftharpoons \underset{\text{membrane pores}}{CO_2(g)}$$

$$\underset{\text{membrane pores}}{CO_2(g)} \rightleftharpoons \underset{\text{internal solution}}{CO_2(aq)}$$

$$\underset{\text{internal solution}}{CO_2(aq)} + 2H_2O \rightleftharpoons \underset{\text{internal solution}}{HCO_3^-} + H_3O^+$$

The last equilibrium causes the pH of the internal surface film to change. This change is then detected by the internal glass/calomel electrode system. A description of the overall process is obtained by adding the equations for the three equilibria to give

$$\underset{\text{analyte solution}}{CO_2(aq)} + 2H_2O \rightleftharpoons \underset{\text{internal solution}}{HCO_3^-} + H_3O^+$$

The thermodynamic equilibrium constant K for this overall reaction is

$$K = \frac{(a_{H_3O^+})_{int}(a_{HCO_3^-})_{int}}{(a_{CO_2})_{ext}}$$

For a neutral species such as CO_2, $a_{CO_2} = [CO_2(aq)]$ so that

$$K = \frac{(a_{H_3O^+})_{int}(a_{HCO_3^-})_{int}}{[CO_2(aq)]_{ext}}$$

where $[CO_2(aq)]_{ext}$ is the molar concentration of the gas in the analyte solution. For the measured cell potential to vary linearly with the logarithm of the carbon dioxide concentration of the external solution, the hydrogen carbonate activity of the internal solution must be sufficiently large that it is not altered significantly by the carbon

dioxide entering from the external solution. Assuming then that $(a_{HCO_3^-})_{int}$ is constant, we can rearrange the previous equations to

$$\frac{(a_{H_3O^+})_{int}}{[CO_2(aq)]_{ext}} = \frac{K}{(a_{HCO_3^-})_{int}} = K_g$$

If we allow a_1 to be the hydrogen ion activity of the internal solution, we rearrange this equation to give

$$(a_{H_3O^+})_{int} = a_1 = K_g[CO_2(aq)]_{ext} \tag{21-15}$$

By substituting Equation 21-15 into Equation 21-10, we find

$$\begin{aligned} E_{ind} &= L + 0.0592 \log a_1 = L + 0.0592 \log K_g[CO_2(aq)]_{ext} \\ &= L + 0.0592 \log K_g + 0.0592 \log [CO_2(aq)]_{ext} \end{aligned}$$

Combining the two constant terms to give a new constant L' leads to

$$E_{ind} = L' + 0.0592 \log [CO_2(aq)]_{ext} \tag{21-16}$$

Finally, since

$$E_{cell} = E_{ind} - E_{ref}$$

then

$$E_{cell} = L' + 0.0592 \log [CO_2(aq)]_{ext} - E_{ref} \tag{21-17}$$

or

$$E_{cell} = L'' + 0.0592 \log [CO_2(aq)]_{ext}$$

where

$$L'' = L + 0.0592 \log K_g - E_{ref}$$

Although sold as gas-sensing electrodes, these devices are complete electrochemical cells and should be called gas-sensing probes.

Thus, the potential between the glass electrode and the reference electrode in the internal solution is determined by the CO_2 concentration in the external solution. Note that no electrode comes in direct contact with the analyte solution. Therefore, these devices are gas-sensing cells, or probes, rather than gas-sensing electrodes. Nevertheless, they continue to be called electrodes is some literature and many advertising brochures.

The only species that interfere are other dissolved gases that permeate the membrane and then affect the pH of the internal solution. The specificity of gas probes depends only on the permeability of the gas membrane. Gas-sensing cells for CO_2, NO_2, H_2S, SO_2, HF, HCN, and NH_3 are now available from commercial sources.

FEATURE 21-3

Point-of-Care Testing: Blood Gases, and Blood Electrolytes with Portable Instrumentation

Modern medicine relies heavily on analytical measurements for diagnosis and treatment in emergency rooms, operating rooms, and intensive care units. Prompt reporting of blood gas values, blood electrolyte concentrations, and other variables is especially important to physicians in these areas. In critical life-and-death situations, there is seldom sufficient time to transport blood samples to the clinical laboratory, perform required analyses, and transmit the results back to the bedside. In this feature, we describe an automated blood gas and electrolyte monitor, designed

specifically to analyze blood samples at the bedside.[7] The iSTAT® Portable Clinical Analyzer, shown in **Figure 21F-4**, is a handheld device that can measure a variety of important clinical analytes such as potassium, sodium, pH, pCO_2, pO_2, and hematocrit (see margin note). In addition, the computer-based analyzer calculates bicarbonate, total carbon dioxide, base excess, O_2 saturation, and hemoglobin in whole blood. In a study of the performance of the iSTAT system in a neonatal and pediatric intensive care unit, the results shown in the following table were obtained.[8] The results were judged to be sufficiently reliable and cost effective to substitute for similar measurements made in a traditional remote clinical laboratory.

Most of the analytes (pCO_2, Na^+, K^+, Ca^{2+}, and pH) are determined by potentiometric measurements using membrane-based ion-selective electrode technology. The hematocrit is measured by electrolytic conductivity detection and pO_2 is determined with a Clark voltammetric sensor (see Section 23C-4). Other results are calculated from these data.

The central component of the monitor is the single-use disposable electrochemical i-STAT sensor array, depicted in **Figure 21F-5**. The individual microfabricated sensor electrodes are located on chips along a narrow flow channel, as shown in the figure. Each new sensor array is automatically calibrated prior to the measurement step.

Hematocrit (Hct) is the ratio of the volume of red blood cells to the total volume of a blood sample expressed as a percent.

Analyte	Range	Precision, %RSD	Resolution
pO_2	5–800 mm Hg	3.5	1 mm Hg
pCO_2	5–130 mm Hg	1.5	0.1 mm Hg
Na^+	100–180 mmol/L	0.4	1 mmol/L
K^+	2.0–9.0 mmol/L	1.2	0.1 mmol/L
Ca^{2+}	0.25–2.50 mmol/L	1.1	0.01 mmol/L
pH	6.5–8.0	0.07	0.001

Figure 21F-4 Photo of iSTAT 1 portable clinical analyzer. (Courtesy of Abbott Point of Care, Inc., Princeton, NJ.)

(*continued*)

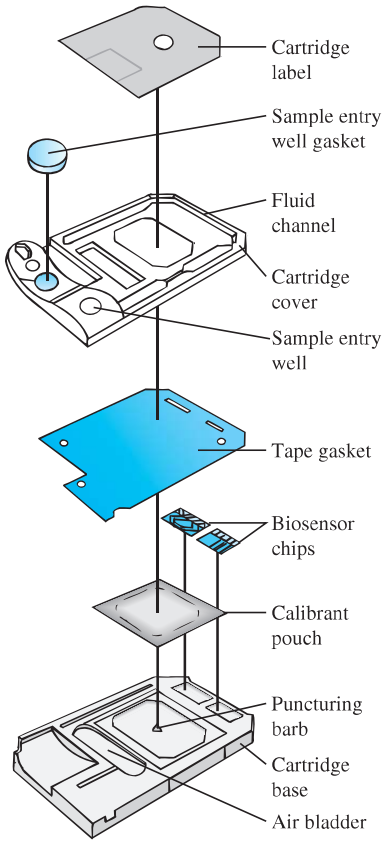


Figure 21F-5 Exploded view of iSTAT sensor array cartridge. (Abbott Point of Care, Prinston, NJ. Reprinted by permission.)

[7]Abbott Point of Care, Inc., Princeton, NJ 08540.

[8]J. N. Murthy, J. M. Hicks, and S. J. Soldin, *Clin. Biochem.*, **1997**, *30,* 385.

A blood sample withdrawn from the patient is deposited into the sample entry well, and the cartridge is inserted into the iSTAT analyzer. The calibrant pouch, which contains a standard buffered solution of the analytes, is punctured by the iSTAT analyzer and compressed to force the calibrant through the flow channel across the surface of the sensor array. When the calibration step is complete, the analyzer compresses the air bladder, which forces the blood sample through the flow channel to expel the calibrant solution to waste and bring the blood into contact with the sensor array. Electrochemical measurements are then made, results are calculated, and the data are presented on the liquid crystal display of the analyzer. The results are stored in the memory of the analyzer and may be transmitted wirelessly to the hospital laboratory data management system for permanent storage and retrieval.

This feature shows how modern ion-selective electrode technology coupled with computer control of the measurement process and data reporting can be used to provide rapid, essential measurements of analyte concentrations in whole blood at a patient's bedside.

21E INSTRUMENTS FOR MEASURING CELL POTENTIAL

Most cells containing a membrane electrode have very high electrical resistance (as much as 10^8 ohms or more). In order to measure potentials of such high-resistance circuits accurately, it is necessary that the voltmeter have an electrical resistance that is several orders of magnitude greater than the resistance of the cell being measured. If the meter resistance is too low, current is drawn from the cell, which has the effect of lowering its output potential, thus creating a negative *loading error*. When the meter and the cell have the same resistance a relative error of −50% results. When this ratio is 10, the error is about −9%. When it is 1000, the error is less than 0.1% relative.

FEATURE 21-4

The Loading Error in Potential Measurements

When we measure voltages in electrical circuits, the meter becomes a part of the circuit, perturbs the measurement process, and produces a **loading error** in the measurement. This situation is not unique to potential measurements. In fact, it is a basic example of a general limitation to any physical measurement. In other words, the process of measurement inevitably disturbs the system of interest so that the quantity actually measured differs from its value prior to the measurement. This type of error can never be completely eliminated, but it can often be reduced to an insignificant level.

The size of the loading error in potential measurements depends on the ratio of the internal resistance of the meter to the resistance of the circuit being studied. The percent relative loading error, E_r, associated with the measured potential, V_M, in Figure 21F-6 is given by

$$E_r = \frac{V_M - V_x}{V_x} \times 100\%$$

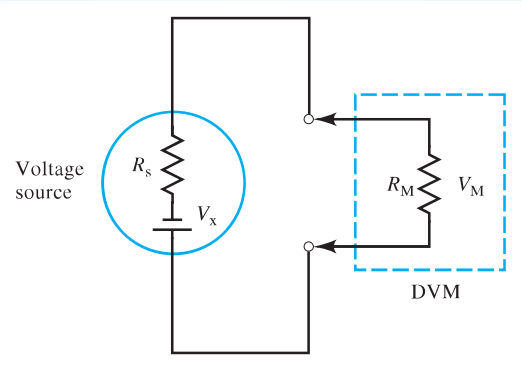


Figure 21F-6 Measurement of output V_x from a potential source with a digital voltmeter.

where V_x is the true voltage of the power source. The voltage drop across the resistance of the meter is given by

$$V_M = V_x \frac{R_M}{R_M + R_s}$$

Substituting this equation into the previous one and rearranging gives

$$E_r = \frac{-R_s}{R_M + R_s} \times 100\%$$

Note in this equation that the relative loading error becomes smaller as the meter resistance, R_M, becomes larger relative to the source resistance R_s. Table 21F-1 illustrates this effect. Digital voltmeters offer the great advantage of having huge internal resistances (10^{11} to 10^{12} ohms), thus avoiding loading errors except in circuits having load resistances greater than about 10^9 ohms.

TABLE 21F-1

Effect of Meter Resistance on the Accuracy of Potential Measurements

Meter Resistance R_M, Ω	Resistance of Source R_s, Ω	R_M/R_s	Relative Error, %
10	20	0.50	−67
50	20	2.5	−29
500	20	25	−3.8
1.0×10^3	20	50	−2.0
1.0×10^4	20	500	−0.2

Numerous high-resistance, direct-reading digital voltmeters with internal resistances of $> 10^{11}$ ohms are now on the market. These meters are commonly called **pH meters** but could more properly be referred to **as pIon meters** or **ion meters** since they are frequently used for the measurement of concentrations of other ions as well. A photo of a typical pH meter is shown in Figure 21-16.

Figure 21-16 Photo of a typical benchtop pH meter. (Courtesy of Mettler Toledo, Inc., Columbus, OH.)

FEATURE 21-5

Operational Amplifier Voltage Measurements

One of the most important developments in chemical instrumentation over the last three decades has been the advent of compact, inexpensive, versatile integrated-circuit amplifiers (op amps).[9] These devices allow us to make potential measurements on high-resistance cells, such as those that contain a glass electrode, without drawing appreciable current. Even a small current (10^{-7}–10^{-10} A) in a glass electrode produces a large error in the measured voltage due to loading (see Feature 21-4) and electrode polarization (see Chapter 22). One of the most important uses for op amps is to isolate voltage sources from their measurement circuits. The basic **voltage follower**, which permits this type of measurement, is shown in **Figure 21F-7a**. This circuit has two important characteristics. The output voltage, E_{out}, is equal to the input voltage, E_{in}, and the input current, I_i, is essentially zero (10^{-7}–10^{-10} A).

A practical application of this circuit is in measuring cell potentials. We simply connect the cell to the op amp input, as shown in **Figure 21F-7b**, and we connect the output of the op amp to a digital voltmeter to measure the voltage. Modern op amps are nearly ideal voltage-measurement devices and are incorporated in most ion meters and pH meters to monitor high-resistance indicator electrodes with minimal error.

Modern ion meters are digital, and some are capable of a precision on the order of 0.001 to 0.005 pH unit. Seldom is it possible to measure pH with a comparable degree of *accuracy*. Inaccuracies of ±0.02 to ±0.03 pH unit are typical.

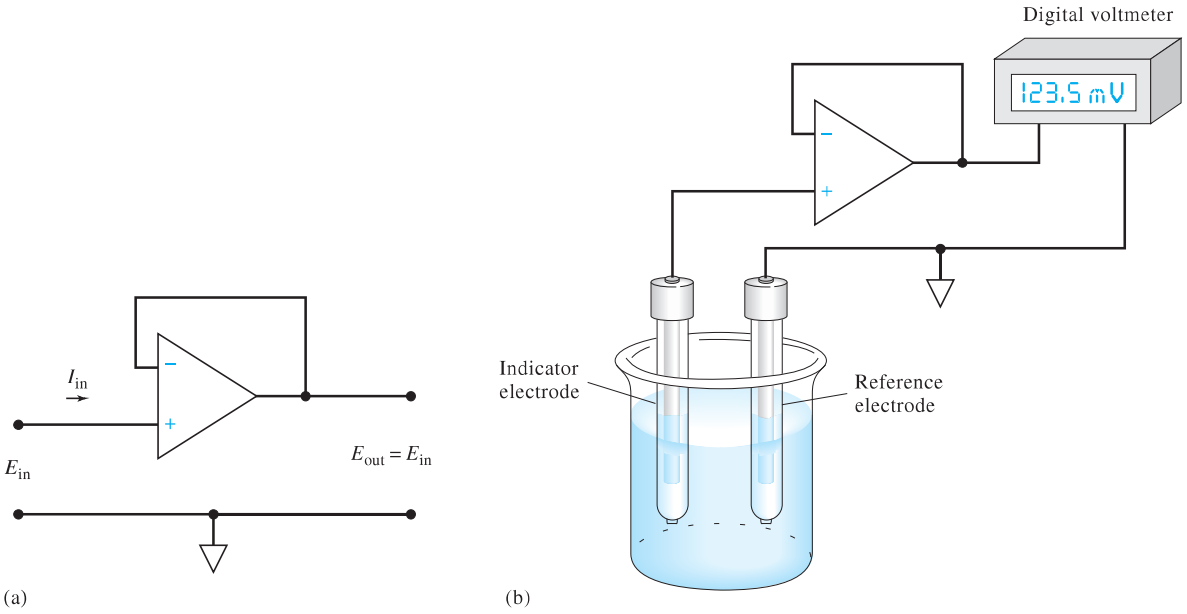


Figure 21F-7 (a) A voltage-follower operational amplifier. (b) Typical arrangement for potentiometric measurements with a membrane electrode.

[9]For a detailed description of op amp circuits, see H. V. Malmstadt, C. G. Enke, and S. R. Crouch, *Microcomputers and Electronic Instrumentation: Making the Right Connections*, Ch. 5, Washington, DC: American Chemical Society, 1994.

21F DIRECT POTENTIOMETRY

Direct potentiometric measurements provide a rapid and convenient method for determining the activity of a variety of cations and anions. The technique requires only a comparison of the potential developed in a cell containing the indicator electrode in the analyte solution with its potential when immersed in one or more standard solutions of known analyte concentration. If the response of the electrode is specific for the analyte, as it often is, no preliminary separation steps are required. Direct potentiometric measurements are also readily adapted to applications requiring continuous and automatic recording of analytical data.

21F-1 Equations Governing Direct Potentiometry

The sign convention for potentiometry is consistent with the convention described in Chapter 18 for standard electrode potential. In this convention, the indicator electrode is always treated as the right-hand electrode and the reference electrode as the left-hand electrode. For direct potentiometric measurements, the potential of a cell can then be expressed in terms of the potentials developed by the indicator electrode, the reference electrode, and a junction potential, as described in Section 21A:

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_{\text{j}} \tag{21-18}$$

In Section 21D, we described the response of various types of indicator electrodes to analyte activities. For the cation X^{n+} at 25°C, the electrode response takes the general *Nernstian* form

$$E_{\text{ind}} = L - \frac{0.0592}{n}\,\text{pX} = L + \frac{0.0592}{n}\log a_{\text{X}} \tag{21-19}$$

where L is a constant and a_{X} is the activity of the cation. For metallic indicator electrodes, L is usually the standard electrode potential; for membrane electrodes, L is the summation of several constants, including the time-dependent asymmetry potential of uncertain magnitude.

Substitution of Equation 21-19 into Equation 21-18 yields with rearrangement

$$\text{pX} = -\log a_{\text{X}} = -\left[\frac{E_{\text{cell}} - (E_{\text{j}} - E_{\text{ref}} + L)}{0.0592/n}\right] \tag{21-20}$$

The constant terms in parentheses can be combined to give a new constant K.

$$\text{pX} = -\log a_{\text{X}} = -\frac{(E_{\text{cell}} - K)}{0.0592/n} = -\frac{n(E_{\text{cell}} - K)}{0.0592} \tag{21-21}$$

For an anion A^{n-}, the sign of Equation 21-21 is reversed:

$$\text{pA} = \frac{(E_{\text{cell}} - K)}{0.0592/n} = \frac{n(E_{\text{cell}} - K)}{0.0592} \tag{21-22}$$

All direct potentiometric methods are based on Equation 21-21 or 21-22. The difference in sign in the two equations has a subtle but important consequence in the

way that ion-selective electrodes are connected to pH meters and pIon meters. When the two equations are solved for E_{cell}, we find that for cations

$$E_{cell} = K - \frac{0.0592}{n} \text{pX} \tag{21-23}$$

and for anions

$$E_{cell} = K + \frac{0.0592}{n} \text{pA} \tag{21-24}$$

Equation 21-23 shows that, for a cation-selective electrode, an increase in pX results in a *decrease* in E_{cell}. Thus, when a high-resistance voltmeter is connected to the cell in the usual way, with the indicator electrode attached to the positive terminal, the meter reading decreases as pX increases. Another way of saying this is that, as the concentration (and activity) of the cation X increases, pX = −log [X] decreases, and E_{cell} increases. Notice that the sense of these changes is exactly the opposite of our sense of how pH meter readings change with increasing hydronium ion concentration. To eliminate this reversal from our sense of the pH scale, instrument manufacturers generally reverse the leads so that cation-sensitive electrodes such as glass electrodes are connected to the negative terminal of the voltage measuring device. Meter readings then increase with increases of pX, and as a result, they decrease with increasing concentration of the cation.

Anion-selective electrodes, on the other hand, are connected to the positive terminal of the meter so that increases in pA also yield larger readings. This sign-reversal conundrum is often confusing so that it is always a good idea to look carefully at the consequences of Equations 21-23 and 21-24 rationalize the output of the instrument with changes in concentration of the analyte anion or cation and corresponding changes in pX or pA.

21F-2 The Electrode-Calibration Method

The electrode-calibration method is also referred to as the method of external standards, which is described in some detail in Section 8D-2.

As we have seen from our discussions in Section 21D, the constant K in Equations 21-21 and 21-22 is made up of several constants, at least one of which, the junction potential, cannot be measured directly or calculated from theory without assumptions. Thus, before these equations can be used for the determination of pX or pA, K must be evaluated experimentally with a standard solution of the analyte.

In the electrode-calibration method, K in Equations 21-21 and 21-22 is determined by measuring E_{cell} for one or more standard solutions of known pX or pA. The assumption is then made that K is unchanged when the standard is replaced by the analyte solution. The calibration is normally performed at the time pX or pA for the unknown is determined. With membrane electrodes, recalibration may be required if measurements extend over several hours because of slow changes in the asymmetry potential.

The electrode-calibration method offers the advantages of simplicity, speed, and applicability to the continuous monitoring of pX or pA. It suffers, however, from a somewhat limited accuracy because of uncertainties in junction potentials.

Inherent Error in the Electrode-Calibration Procedure

A serious disadvantage of the electrode-calibration method is the inherent error that results from the assumption that K in Equations 21-21 and 21-22 remains constant after calibration. This assumption can seldom, if ever, be exactly true because the

electrolyte composition of the unknown almost inevitably differs from that of the solution used for calibration. The junction potential term contained in K varies slightly as a consequence, even when a salt bridge is used. This error is frequently on the order of 1 mV or more. Unfortunately, because of the nature of the potential/activity relationship, such an uncertainty has an amplified effect on the inherent accuracy of the analysis.

The magnitude of the error in analyte concentration can be estimated by differentiating Equation 21-21 while assuming E_{cell} constant.

$$-\log_{10} e \frac{da_x}{a_x} = -0.434 \frac{da_x}{a_x} = -\frac{dK}{0.0592/n}$$

$$\frac{da_x}{a_x} = \frac{ndK}{0.0257} = 38.9\, ndK$$

When we replace da_x and dK with finite increments and multiply both sides of the equation by 100%, we obtain

$$\text{percent relative error} = \frac{\Delta a_x}{a_x} \times 100\% = 38.9 n\Delta K \times 100\%$$
$$= 3.89 \times 10^3 n\Delta K\% \approx 4000 n\Delta K\%$$

The quantity $\Delta a_x/a_x$ is the relative error in a_x associated with an absolute uncertainty ΔK in K. If, for example, ΔK is ± 0.001 V, a relative error in activity of about $\pm 4n\%$ can be expected. *It is important to appreciate that this error is characteristic of all measurements involving cells that contain a salt bridge and that this error cannot be eliminated by even the most careful measurements of cell potentials or the most sensitive and precise measuring devices.*

Activity versus Concentration

Electrode response is related to analyte activity rather than analyte concentration. We are usually interested in concentration, however, and the determination of this quantity from a potentiometric measurement requires activity coefficient data. Activity coefficients are seldom available because the ionic strength of the solution either is unknown or else is so large that the Debye-Hückel equation is not applicable.

The difference between activity and concentration is illustrated by **Figure 21-17** in which the response of a calcium ion electrode is plotted against a logarithmic

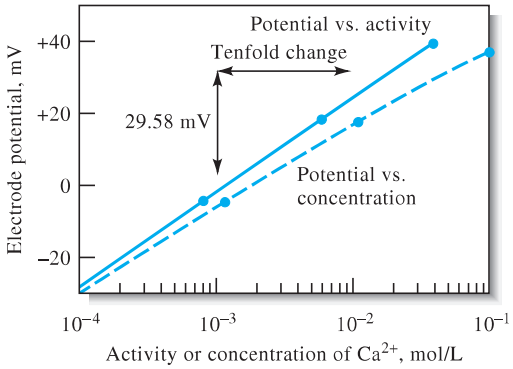


Figure 21-17 Response of a liquid-membrane electrode to variations in the concentration and activity of calcium ion. (Courtesy of Thermo Electron Corp., Beverly, MA.)

function of calcium chloride concentration. The nonlinearity is due to the increase in ionic strength—and the consequent decrease in the activity of calcium ion—with increasing electrolyte concentration. The upper curve is obtained when these concentrations are converted to activities. This straight line has the theoretical slope of 0.0296 (0.0592/2).

Activity coefficients for singly charged species are less affected by changes in ionic strength than are the coefficients for ions with multiple charges. Thus, the effect shown in Figure 21-17 is less pronounced for electrodes that respond to H^+, Na^+, and other univalent ions.

Many chemical reactions of physiological importance depend on the activity of metal ions rather than their concentration.

In potentiometric pH measurements, the pH of the standard buffer used for calibration is generally based on the activity of hydrogen ions. Therefore, the results are also on an activity scale. If the unknown sample has a high ionic strength, the hydrogen ion *concentration* will differ appreciably from the activity measured.

An obvious way to convert potentiometric measurements from activity to concentration is to make use of an empirical calibration curve, such as the lower plot in Figure 21-17. For this approach to be successful, it is necessary to make the ionic composition of the standards essentially the same as that of the analyte solution. Matching the ionic strength of standards to that of samples is often difficult, particularly for samples that are chemically complex.

A total ionic strength adjustment buffer (TISAB) is used to control the ionic strength and the pH of samples and standards, in ion-selective electrode measurements.

Where electrolyte concentrations are not too great, it is often useful to swamp both samples and standards with a measured excess of an inert electrolyte. The added effect of the electrolyte from the sample matrix becomes negligible under these circumstances, and the empirical calibration curve yields results in terms of concentration. This approach has been used, for example, in the potentiometric determination of fluoride ion in drinking water. Both samples and standards are diluted with a solution that contains sodium chloride, an acetate buffer, and a citrate buffer; the diluent is sufficiently concentrated so that the samples and standards have essentially identical ionic strengths. This method provides a rapid means for measuring fluoride concentrations in the part-per-million range with an accuracy of about 5% relative.

21F-3 The Standard Addition Method

The standard addition method (see Section 8D-3) involves determining the potential of the electrode system before and after a measured volume of a standard has been added to a known volume of the analyte solution. Multiple additions can also be made. Often, an excess of an electrolyte is introduced into the analyte solution to prevent any major shift in ionic strength that might accompany the addition of standard. It is also necessary to assume that the junction potential remains constant during the two measurements.

EXAMPLE 21-1

A cell consisting of a saturated calomel electrode and a lead ion electrode developed a potential of −0.4706 V when immersed in 50.00 mL of a sample. A 5.00-mL addition of standard 0.02000 M lead solution caused the potential to shift to −0.4490 V. Calculate the molar concentration of lead in the sample.

Solution

We shall assume that the activity of Pb^{2+} is approximately equal to $[Pb^{2+}]$ and apply Equation 21-21. Thus,

$$pPb = -\log [Pb^{2+}] = -\frac{E'_{cell} - K}{0.0592/2}$$

where E'_{cell} is the initial measured potential (−0.4706 V).

After the standard solution is added, the potential becomes E''_{cell} (−0.4490 V), and

$$-\log \frac{50.00 \times [Pb^{2+}] + 5.00 \times 0.0200}{50.00 + 5.00} = -\frac{E''_{cell} - K}{0.0592/2}$$

$$-\log(0.9091[Pb^{2+}] + 1.818 \times 10^{-3}) = -\frac{E''_{cell} - K}{0.0592/2}$$

Subtracting this equation from the first leads to

$$-\log \frac{[Pb^{2+}]}{0.09091[Pb^{2+}] + 1.818 \times 10^{-3}} = \frac{2(E''_{cell} - E'_{cell})}{0.0592}$$

$$= \frac{2[-0.4490 - (-0.4706)]}{0.0592}$$

$$= 0.7297$$

$$\frac{[Pb^{2+}]}{0.09091[Pb^{2+}] + 1.818 \times 10^{-3}} = \text{antilog}(-0.7297) = 0.1863$$

$$[Pb^{2+}] = 3.45 \times 10^{-4}\ M$$

21F-4 Potentiometric pH Measurement with the Glass Electrode[10]

The glass electrode is unquestionably the most important indicator electrode for hydrogen ion. It is convenient to use and subject to few of the interferences that affect other pH-sensing electrodes.

The glass/calomel electrode system is a remarkably versatile tool for the measurement of pH under many conditions. It can be used without interference in solutions containing strong oxidants, strong reductants, proteins, and gases; the pH of viscous or even semisolid fluids can be determined. Electrodes for special applications are available. Included among these electrodes are small ones for pH measurements in one drop (or less) of solution, in a tooth cavity, or in the sweat on the skin; microelectrodes that permit the measurement of pH inside a living cell; rugged electrodes for insertion in a flowing liquid stream to provide a continuous monitoring of pH; and small electrodes that can be swallowed to measure the acidity of the stomach contents (the calomel electrode is kept in the mouth).

Errors Affecting pH Measurements

The ubiquity of the pH meter and the general applicability of the glass electrode tend to lull the chemist into the attitude that any measurement obtained with such

[10]For a detailed discussion of potentiometric pH measurements, see R. G. Bates, *Determination of pH*, 2nd ed., New York: Wiley, 1973.

equipment is surely correct. The reader must be alert to the fact that there are distinct limitations to the electrode, some of which were discussed in earlier sections:

1. *The alkaline error*. The ordinary glass electrode becomes somewhat sensitive to alkali metal ions and gives low readings at pH values greater than 9.
2. *The acid error*. Values registered by the glass electrode tend to be somewhat high when the pH is less than about 0.5.
3. *Dehydration*. Dehydration may cause erratic electrode performance.
4. *Errors in low ionic strength solutions*. It has been found that significant errors (as much as 1 or 2 pH units) may occur when the pH of samples of low ionic strength, such as lake or stream water, is measured with a glass/calomel electrode system.[11] The prime source of such errors has been shown to be nonreproducible junction potentials, which apparently result from partial clogging of the fritted plug or porous fiber that is used to restrict the flow of liquid from the salt bridge into the analyte solution. To overcome this problem, free diffusion junctions of various types have been designed, one of which is produced commercially.
5. *Variation in junction potential*. A fundamental source of uncertainty for which a correction cannot be applied is the junction-potential variation resulting from differences in the composition of the standard and the unknown solution.
6. *Error in the pH of the standard buffer*. Any inaccuracies in the preparation of the buffer used for calibration or any changes in its composition during storage cause an error in subsequent pH measurements. The action of bacteria on organic buffer components is a common cause for deterioration.

Particular care must be taken in measuring the pH of approximately neutral unbuffered solutions, such as samples from lakes and streams.

The Operational Definition of pH

Perhaps the most common analytical instrumental technique is the measurement of pH.

The utility of pH as a measure of the acidity and alkalinity of aqueous media, the wide availability of commercial glass electrodes, and the relatively recent proliferation of inexpensive solid-state pH meters have made the potentiometric measurement of pH perhaps the most common analytical technique in all of science. It is thus extremely important that pH be defined in a manner that is easily duplicated at various times and in various laboratories throughout the world. To meet this requirement, it is necessary to define pH in operational terms, that is, by the way the measurement is made. Only then will the pH measured by one worker be the same as that by another.

By definition, pH is what you measure with a glass electrode and a pH meter. It is approximately equal to the theoretical definition of $pH = -\log a_{H^+}$.

The operational definition of pH is endorsed by the National Institute of Standards and Technology (NIST), similar organizations in other countries, and the IUPAC. It is based on the direct calibration of the meter with carefully prescribed standard buffers followed by potentiometric determination of the pH of unknown solutions.

Consider, for example, one of the glass/reference electrode pairs of Figure 21-7. When these electrodes are immersed in a standard buffer, Equation 21-21 applies, and we can write

$$pH_S = \frac{E_S - K}{0.0592}$$

[11] See W. Davison and C. Woof, *Anal. Chem.*, **1985**, *57*, 2567, **DOI**: 10.1021/ac00290a031; T. R. Harbinson and W. Davison, *Anal. Chem.*, **1987**, *59*, 2450, **DOI**: 10.1021/ac00147a002.

where E_S is the cell potential when the electrodes are immersed in the buffer. Similarly, if the cell potential is E_U when the electrodes are immersed in a solution of unknown pH, we have

$$pH_U = -\frac{E_U - K}{0.0592}$$

By subtracting the first equation from the second and solving for pH_U, we find

$$pH_U = pH_S - \frac{(E_U - E_S)}{0.0592} \qquad (21\text{-}25)$$

Equation 21-25 has been adopted throughout the world as the *operational definition of pH*.

An operational definition of a quantity defines the quantity in terms of how it is measured.

Workers at the NIST and elsewhere have used cells without liquid junctions to study primary-standard buffers extensively. Some of the properties of these buffers are discussed in detail elsewhere.[12] Note that the NIST buffers are described by their molal concentrations (mol solute/kg solvent) for accuracy and precision of preparation. For general use, the buffers can be prepared from relatively inexpensive laboratory reagents; for careful work, however, certified buffers can be purchased from the NIST.

It should be emphasized that the strength of the operational definition of pH is that it provides a coherent scale for the determination of acidity or alkalinity. However, measured pH values cannot be expected to yield a detailed picture of solution composition that is entirely consistent with solution theory. This uncertainty stems from our fundamental inability to measure single ion activities, that is, the operational definition of pH does not yield the exact pH as defined by the equation

$$pH = -\log \gamma_{H^+}[H^+]$$

21G POTENTIOMETRIC TITRATIONS

In a **potentiometric titration**, we measure the potential of a suitable indicator electrode as a function of titrant volume. The information provided by a potentiometric titration is different from the data obtained in a direct potentiometric measurement. For example, the direct measurement of 0.100 M solutions of hydrochloric and acetic acids yields two substantially different hydrogen ion concentrations because the weak acid is only partially dissociated. In contrast, the potentiometric titration of equal volumes of the two acids would require the same amount of standard base because both solutes have the same number of titratable protons.

Potentiometric titrations provide data that are more reliable than data from titrations that use chemical indicators and are particularly useful with colored or turbid solutions and for detecting the presence of unsuspected species. Potentiometric titrations have been automated in a variety of different ways, and commercial titrators are available from a number of manufacturers. Manual potentiometric titrations, on the other hand, suffer from the disadvantage of being more time consuming than those involving indicators.

[12]R. G. Bates, *Determination of pH*, 2nd ed., Ch. 4., New York: Wiley, 1973.

Automatic *titrators* for carrying out potentiometric titrations are available from several manufacturers. The operator of the instrument simply adds the sample to the titration vessel and pushes a button to initiate, the titration. The instrument adds titrant, records the potential versus volume data, and analyzes the data to determine the concentration of the unknown solution. A photo of such a device is shown on the opening page of Chapter 14.

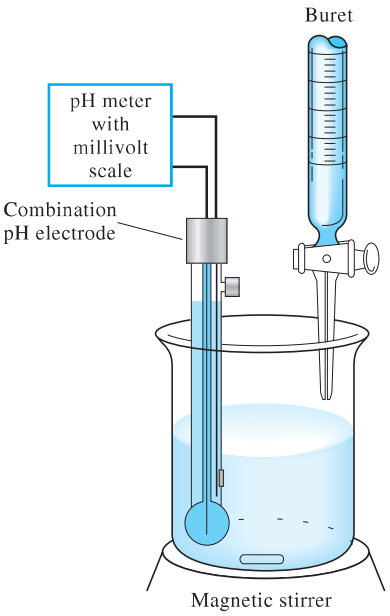


Figure 21-18 Apparatus for a potentiometric titration.

Potentiometric titrations offer additional advantages over direct potentiometry. Because the measurement is based on the titrant volume that causes a rapid *change* in potential near the equivalence point, potentiometric titrations are not dependent on measuring absolute values of E_{cell}. This characteristic makes the titration relatively free from junction potential uncertainties because the junction potential remains approximately constant during the titration. Titration results, instead, depend most heavily on having a titrant of accurately known concentration. The potentiometric instrument merely signals the end point and thus behaves in an identical fashion to a chemical indicator. Problems with electrodes fouling or not displaying Nernstian response are not nearly as serious when the electrode system is used to monitor a titration. Likewise, the reference electrode potential does not need to be known accurately in a potentiometric titration. Another advantage of a titration is that the result is analyte concentration even though the electrode responds to activity. For this reason, ionic strength effects are not important in the titration procedure.

Figure 21-18 illustrate a typical apparatus for performing a manual potentiometric titration. The operator measures and records the cell potential (in units of millivolts or pH, as appropriate) after each addition of reagent. The titrant is added in large increments early in the titration and in smaller and smaller increments as the end point is approached (as indicated by larger changes in cell potential per unit volume).

21G-1 Detecting the End Point

Several methods can be used to determine the end point of a potentiometric titration. In the most straightforward approach, a direct plot or other recording is made of cell potential as a function of reagent volume. In Figure 21-19a, we plot the data of Table 21-4 and visually estimate the inflection point in the steeply rising portion of the curve and take it as the end point.

TABLE 21-4

Potentiometric Titration Data for 2.433 mmol of Chloride with 0.1000 M Silver Nitrate

Volume $AgNO_3$, mL	E vs. SCE, V	$\Delta E/\Delta V$, V/mL	$\Delta^2 E/\Delta V^2$, V^2/mL^2
5.00	0.062		
15.00	0.085	0.002	
20.00	0.107	0.004	
22.00	0.123	0.008	
23.00	0.138	0.015	
23.50	0.146	0.016	
23.80	0.161	0.050	
24.00	0.174	0.065	
24.10	0.183	0.09	
24.20	0.194	0.11	2.8
24.30	0.233	0.39	4.4
24.40	0.316	0.83	−5.9
24.50	0.340	0.24	−1.3
24.60	0.351	0.11	−0.4
24.70	0.358	0.07	
25.00	0.373	0.050	
25.50	0.385	0.024	
26.00	0.396	0.022	
28.00	0.426	0.015	

A second approach to end-point detection is to calculate the change in potential per unit volume of titrant ($\Delta E/\Delta V$), that is, we estimate the numerical first derivative of the titration curve. A plot of the first derivative data (see Table 21-4, column 3) as a function of the average volume V produces a curve with a maximum that corresponds to the point of inflection, as shown in **Figure 21-19b**. Alternatively, this ratio can be evaluated during the titration and recorded rather than the potential. From the plot, it can be seen that the maximum occurs at a titrant volume of about 24.30 mL. If the titration curve is symmetrical, the point of maximum slope coincides with the equivalence point. For the asymmetrical titration curves that are observed when the titrant and analyte half-reactions involve different numbers of electrons, a small titration error occurs if the point of maximum slope is used.

Figure 21-19c shows that the second derivative for the data changes sign at the point of inflection. This change is used as the analytical signal in some automatic titrators. The point at which the second derivative crosses zero is the inflection point, which is taken as the end point of the titration, and this point can be located quite precisely.

All of the methods of end-point detection discussed in the previous paragraphs are based on the assumption that the titration curve is symmetric about the equivalence point and that the inflection in the curve corresponds to this point. This assumption is valid if the titrant and analyte react in a 1:1 ratio and if the electrode reaction is reversible. Many oxidation/reduction reactions, such as the reaction of iron(II) with permanganate, do not occur in equimolar fashion. Even so, such titration curves are often so steep at the end point that very little error is introduced by assuming that the curves are symmetrical.

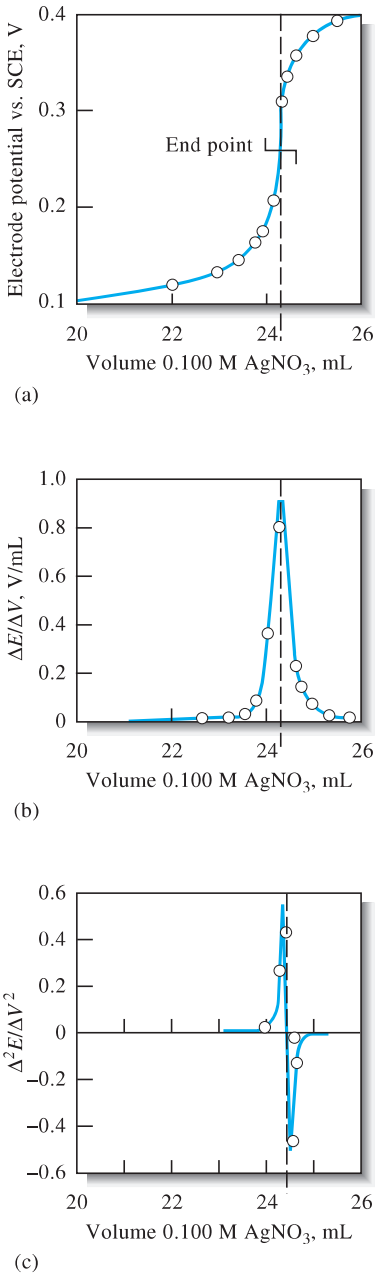


Figure 21-19 Titration of 2.433 mmol of chloride ion with 0.1000 M silver nitrate. (a) Titration curve. (b) First-derivative curve. (c) Second-derivative curve.

21G-2 Neutralization Titrations

Experimental neutralization curves closely approximate the theoretical curves described in Chapters 14 and 15. Usually, the experimental curves are somewhat displaced from the theoretical curves along the pH axis because concentrations rather than activities are used in their derivation. This displacement has little effect on determining end points, and so potentiometric neutralization titrations are quite useful for analyzing mixtures of acids or polyprotic acids. The same is true of bases.

Determining Dissociation Constants

An approximate numerical value for the dissociation constant of a weak acid or base can be estimated from potentiometric titration curves. This quantity can be computed from the pH at any point along the curve, but a very convenient point is the half-titration point. At this point on the curve,

$$[HA] \approx [A^-]$$

Therefore,

$$K_a = \frac{[H_3O^+]\cancel{[A^-]}}{\cancel{[HA]}} = [H_3O^+]$$

$$pK_a = pH$$

It is important to note the use of concentrations instead of activities may cause the value for K_a to differ from its published value by a factor of 2 or more. A more correct form of the dissociation constant for HA is

$$K_a = \frac{a_{H_3O^+} a_{A^-}}{a_{HA}} = \frac{a_{H_3O^+} \gamma_{A^-} [A^-]}{\gamma_{HA} [HA]} \tag{21-26}$$

$$K_a = \frac{a_{H_3O^+} \gamma_{A^-}}{\gamma_{HA}}$$

Since the glass electrode provides a good approximation of $a_{H_3O^+}$, the measured value of K_a differs from the thermodynamic value by the ratio of the two activity coefficients. The activity coefficient in the denominator of Equation 21-26 doesn't change significantly as ionic strength increases because HA is a neutral species. The activity coefficient for A^-, on the other hand, decreases as the electrolyte concentration increases. This decrease means that the observed hydrogen ion activity must be numerically larger than the thermodynamic dissociation constant.

EXAMPLE 21-2

In order to determine K_1 and K_2 for H_3PO_4 from titration data, careful pH measurements are made after 0.5 and 1.5 mol of base is added for each mole of acid. It is then assumed that the hydrogen ion activities computed from these data are identical to the desired dissociation constants. Calculate the relative error incurred by the assumption if the ionic strength is 0.1 at the time of each measurement. (From Appendix 3, K_1 and K_2 for H_3PO_4 are 7.11×10^{-3} and 6.34×10^{-8}, respectively.)

Solution

If we rearrange Equation 21-26, we find that

$$K_a(\text{exptl}) = a_{H_3O^+} = K\left(\frac{\gamma_{HA}}{\gamma_{A^-}}\right)$$

The activity coefficient for H_3PO_4 is approximately equal to 1 since the free acid has no charge. In Table 10-2, we find that the activity coefficient for $H_2PO_4^-$ is 0.77 and that for HPO_4^{2-} is 0.35. When we substitute these values into the equations for K_1 and K_2, we find that

$$K_1(\text{exptl}) = 7.11 \times 10^{-3}\left(\frac{1.00}{0.77}\right) = 9.23 \times 10^{-3}$$

$$\text{error} = \frac{9.23 \times 10^{-3} - 7.11 \times 10^{-3}}{7.11 \times 10^{-3}} \times 100\% = 30\%$$

$$K_2(\text{exptl}) = 6.34 \times 10^{-8}\left(\frac{0.77}{0.35}\right) = 1.395 \times 10^{-7}$$

$$\text{error} = \frac{1.395 \times 10^{-7} - 6.34 \times 10^{-8}}{6.34 \times 10^{-8}} \times 100\% = 120\%$$

It is possible to identify an unknown pure acid by performing a single titration to determine its equivalent mass (molar mass if the acid is monoprotic) and its dissociation constant.

21G-3 Oxidation/Reduction Titrations

An inert indicator electrode constructed of platinum is usually used to detect end points in oxidation/reduction titrations. Occasionally, other inert metals, such a silver, palladium, gold, and mercury, are used instead. Titration curves similar to those constructed in Section 19D are usually obtained, although they may be displaced along the potential (vertical) axis as a consequence of the high ionic strengths. End points are determined by the methods described earlier in this chapter.

21H POTENTIOMETRIC DETERMINATION OF EQUILIBRIUM CONSTANTS

Numerical values for solubility-product constants, dissociation constants, and formation constants are conveniently evaluated through the measurement of cell potentials. One important virtue of this technique is that the measurement can be made without appreciably affecting any equilibria that may be present in the solution. For example, the potential of a silver electrode in a solution containing silver ion, cyanide ion, and the complex formed between them depends on the activities of the three species. It is possible to measure this potential with negligible current. Since the activities of the participants are not altered during the measurement, the position of the equilibrium

$$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$$

is likewise undisturbed.

EXAMPLE 21-3

Calculate the formation constant K_f for $Ag(CN)_2^-$:

$$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$$

if the cell

$$SCE \,\|\, Ag(CN)_2^- (7.50 \times 10^{-3}\ M),\ CN^- (0.0250\ M) \,|\, Ag$$

develops a potential of −0.625 V.

Solution

Proceeding as in the earlier examples, we have

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad E^0 = +0.799\ V$$

$$-0.625 = E_{right} - E_{left} = E_{Ag^+} - 0.244$$

$$E_{Ag^+} = -0.625 + 0.244 = -0.381\ V$$

(*continued*)

We then apply the Nernst equation for the silver electrode to find that

$$-0.381 = 0.799 - \frac{0.0592}{1}\log\frac{1}{[Ag^+]}$$

$$\log[Ag^+] = \frac{-0.381 - 0.799}{0.0592} = -19.93$$

$$[Ag^+] = 1.2 \times 10^{-20}$$

$$K_f = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = \frac{7.50 \times 10^{-3}}{(1.2 \times 10^{-20})(2.5 \times 10^{-2})^2}$$

$$= 1.0 \times 10^{21} \approx 1 \times 10^{21}$$

In theory, any electrode system in which hydrogen ions are participants can be used to evaluate dissociation constants for acids and bases.

EXAMPLE 21-4

Calculate the dissociation constant K_{HP} for the weak acid HP if the cell

$$SCE \,\|\, HP(0.010\ M), NaP(0.040\ M) \,|\, Pt, H_2\ (1.00\ atm)$$

develops a potential of −0.591 V.

Solution

The diagram for this cell indicates that the saturated calomel electrode is the left-hand electrode. Thus,

$$E_{cell} = E_{right} - E_{left} = E_{right} - 0.244 = -0.591\ V$$

$$E_{right} = -0.591 + 0.244 = -0.347\ V$$

We then apply the Nernst equation for the hydrogen electrode to find that

$$-0.347 = 0.000 - \frac{0.0592}{2}\log\frac{1.00}{[H_3O^+]^2}$$

$$= 0.000 + \frac{2 \times 0.0592}{2}\log[H_3O^+]$$

$$\log[H_3O^+] = \frac{-0.347 - 0.000}{0.0592} = -5.86$$

$$[H_3O^+] = 1.38 \times 10^{-6}$$

By substituting this value of the hydronium ion concentration as well as the concentrations of the weak acid and its conjugate base into the dissociation constant expression, we obtain

$$K_{HP} = \frac{[H_3O^+][P^-]}{HP} = \frac{(1.38 \times 10^{-6})(0.040)}{0.010} = 5.5 \times 10^{-6}$$

WEB WORKS

Use a Web search engine, such as Google, to find sites dealing with potentiometric titrators. This search should turn up such companies as Spectralab, Analyticon, Fox Scientific, Metrohm, Mettler-Toledo, and Thermo Orion. Set your browser to one or two of these and explore the types of titrators that are commercially available. At the sites of two different manufacturers, find application notes or bulletins for determining two analytes by potentiometric titration. For each, list the analyte, the instruments and the reagents that are necessary for the determination, and the expected accuracy and precision of the results. Describe the detailed chemistry behind each determination and the experimental procedure.

QUESTIONS AND PROBLEMS

21-1. Briefly describe or define
- *(a) indicator electrode.
- (b) reference electrode.
- *(c) electrode of the first kind.
- (d) electrode of the second kind.

21-2. Briefly describe or define
- *(a) liquid-junction potential.
- (b) boundary potential.
- *(c) asymmetry potential.
- (d) combination electrode.

***21-3.** You need to choose between determining an analyte by measuring an electrode potential or by performing a titration. Explain which you would choose if you needed to know
- (a) the absolute amount of the analyte to a few parts per thousand.
- (b) the activity of the analyte.

21-4. What is meant by Nernstian behavior in an indicator electrode?

***21-5.** Describe the source of pH dependence in a glass membrane electrode.

21-6. Why is it necessary for the glass in the membrane of a pH-sensitive electrode to be appreciably hygroscopic?

***21-7.** List several sources of uncertainty in pH measurements with a glass/calomel electrode system.

21-8. What experimental factor places a limit on the number of significant figures in the response of a membrane electrode?

***21-9.** Describe the alkaline error in the measurement of pH. Under what circumstances is this error appreciable? How are pH data affected by alkaline error?

21-10. How does a gas-sensing probe differ from other membrane electrodes?

21-11. What is the source of
- (a) the asymmetry potential in a membrane electrode?
- *(b) the boundary potential in a membrane electrode?
- (c) a junction potential in a glass/calomel electrode system?
- *(d) the potential of a crystalline membrane electrode used to determine the concentration of F^-?

***21-12.** How does information supplied by a direct potentiometric measurements of pH differ from that obtained from a potentiometric acid/base titration?

21-13. Give several advantages of a potentiometric titration over a direct potentiometric measurement.

21-14. What is the "operational definition of pH"? Why is it used?

***21-15.** (a) Calculate E^0 for the process

$$AgIO_3(s) + e^- \rightleftharpoons Ag(s) + IO_3^-$$

- (b) Use the shorthand notation to describe a cell consisting of a saturated calomel reference electrode and a silver indicator electrode that could be used to measure pIO_3.
- (c) Develop an equation that relates the potential of the cell in (b) to pIO_3.
- (d) Calculate pIO_3 if the cell in (b) has a potential of 0.306 V.

21-16. (a) Calculate E^0 for the process

$$PbI_2(s) + e^- \rightleftharpoons Pb(s) + 2I^-$$

- (b) Use the shorthand notation to describe a cell consisting of a saturated calomel reference electrode and a lead indicator electrode that could be used for the measurement of pI.
- (c) Generate an equation that relates the potential of this cell to pI.
- (d) Calculate pI if this cell has a potential of −0.402 V.

21-17. Use the shorthand notation to describe a cell consisting of a saturated calomel reference electrode and a silver indicator electrode for the measurement of
- *(a) pI.
- (b) pSCN.
- *(c) pPO_4.
- (d) pSO_3.

21-18. Generate an equation that relates pAnion to E_{cell} for each of the cells in Problem 21-17. (For Ag_2SO_3, $K_{sp} = 1.5 \times 10^{-14}$; for Ag_3PO_4, $K_{sp} = 1.3 \times 10^{-20}$.)

21-19. Calculate

*(a) pI if the cell in Problem 21-17(a) has a potential of −196 mV.

(b) pSCN if the cell in Problem 21-17(b) has a potential of 0.137 V.

*(c) pPO_4 if the cell in Problem 21-17(c) has a potential of 0.211 V.

(d) pSO_3 if the cell in Problem 21-17(d) has a potential of 285 mV.

***21-20.** The cell

$$SCE\|Ag_2CrO_4(sat'd), (x\ M)|Ag$$

is used for the determination of $pCrO_4$. Calculate $pCrO_4$ when the cell potential is 0.389 V.

***21-21.** The cell

$$SCE\|H^+(a = x)|\text{glass electrode}$$

has a potential of 0.2106 V when the solution in the right-hand compartment is a buffer of pH 4.006. The following potentials are obtained when the buffer is replaced with unknowns: (a) −0.2902 V and (b) +0.1241 V. Calculate the pH and the hydrogen ion activity of each unknown. (c) Assuming an uncertainty of 0.002 V in the junction potential, what is the range of hydrogen ion activities within which the true value might be expected to lie?

***21-22.** A 0.4021-g sample of a purified organic acid was dissolved in water and titrated potentiometrically. A plot of the data revealed a single end point after 18.62 mL of 0.1243 M NaOH had been introduced. Calculate the molecular mass of the acid.

21-23. Calculate the potential of a silver indicator electrode versus the standard calomel electrode after the addition of 5.00, 15.00, 25.00, 30.00, 35.00, 39.00, 39.50, 36.60, 39.70, 39.80, 39.90, 39.95, 39.99, 40.00, 40.01, 40.05, 40.10, 40.20, 40.30, 40.40, 40.50, 41.00, 45.00, 50.00, 55.00, and 70.00 mL of 0.1000 M $AgNO_3$ to 50.00 mL of 0.0800 M KSeCN. Construct a titration curve and a first and second derivative plot from these data. (K_{sp} for AgSeCN = 4.20×10^{-16}.)

21-24. A 40.00-mL aliquot of 0.05000 M HNO_2 is diluted to 75.00 mL and titrated with 0.0800 M Ce^{4+}. The pH of the solution is maintained at 1.00 throughout the titration; the formal potential of the cerium system is 1.44 V.

(a) Calculate the potential of the indicator electrode with respect to a saturated calomel reference electrode after the addition of 5.00, 10.00, 15.00, 25.00, 40.00, 49.00, 49.50, 49.60, 49.70, 49.80, 49.90, 49.95, 49.99, 50.00, 50.01, 50.05, 50.10, 50.20, 50.30, 50.40, 50.50, 51.00, 60.00, 75.00, and 90.00 mL of cerium(IV).

(b) Draw a titration curve for these data.

(c) Generate a first and second derivative curve for these data. Does the volume at which the second derivative curve crosses zero correspond to the theoretical equivalence point? Why or why not?

21-25. The titration of Fe(II) with permanganate yields a particularly asymmetrical titration curve because of the different number of electrons involved in the two half-reactions. Consider the titration of 25.00 mL of 0.1 M Fe(II) with 0.1 M MnO_4^-. The H^+ concentration is maintained at 1.0 M throughout the titration. Use a spreadsheet to generate a theoretical titration curve and a first and second derivative plot. Do the inflection points obtained from the maximum of the first derivative plot or the zero crossing of the second derivative plot correspond to the equivalence point? Explain why or why not.

***21-26.** The Na^+ concentration of a solution was determined by measurements with a sodium ion-selective electrode. The electrode system developed a potential of −0.2462 V when immersed in 10.0 mL of the solution of unknown concentration. After addition of 1.00 mL of 2.00×10^{-2} M NaCl, the potential changed to −0.1994 V. Calculate the Na^+ concentration of the original solution.

21-27. The F^- concentration of a solution was determined by measurements with a liquid-membrane electrode. The electrode system developed a potential of 0.5021 V when immersed in 25.00 mL of the sample, and 0.4213 V after the addition of 2.00 mL of 5.45×10^{-2} M NaF. Calculate pF for the sample.

21-28. A lithium ion-selective electrode gave the potentials given below for the following standard solutions of LiCl and two samples of unknown concentration:

Solution (a_{Li^+})	Potential vs. SCE, mV
0.100 M	+1.0
0.050 M	−30.0
0.010 M	−60.0
0.001 M	−138.0
Unknown 1	−48.5
Unknown 2	−75.3

(a) Construct a calibration curve of potential versus $\log a_{Li^+}$ and determine if the electrode follows the Nernst equation.

(b) Use a linear least-squares procedure to determine the concentrations of the two unknowns.

21-29. A fluoride electrode was used to determine the amount of fluoride in drinking water samples. The results given in the table below were obtained for four standards and two unknowns. Constant ionic strength and pH conditions were used.

Solution Containing F^-	Potential vs. SCE, mV
5.00×10^{-4} M	0.02
1.00×10^{-4} M	41.4
5.00×10^{-5} M	61.5
1.00×10^{-5} M	100.2
Unknown 1	38.9
Unknown 2	55.3

(a) Plot a calibration curve of potential versus log[F^-]. Determine whether the electrode system shows Nernstian response.

(b) Determine the concentration of F^- in the two unknown samples by a linear least-squares procedure.

21-30. Challenge Problem: Ceresa, Pretsch, and Bakker[13] investigated three ion-selective electrodes for determining calcium concentrations. All three electrodes used the same membrane but differed in the composition of the inner solution. Electrode 1 was a conventional ISE with an inner solution of 1.00×10^{-3} M $CaCl_2$ and 0.10 M NaCl. Electrode 2 (low activity of Ca^{2+}) had an inner solution containing the same analytical concentration of $CaCl_2$, but with 5.0×10^{-2} M EDTA adjusted to a pH of 9.0 with 6.0×10^{-2} M NaOH. Electrode 3 (high Ca^{2+} activity) had an inner solution of 1.00 M $Ca(NO_3)_2$.

(a) Determine the Ca^{2+} concentration in the inner solution of Electrode 2.

(b) Determine the ionic strength of the solution in Electrode 2.

(c) Use the Debye-Hückel equation and determine the activity of Ca^{2+} in Electrode 2. Use 0.6 nm for the α_X value for Ca^{2+}.

(d) Electrode 1 was used in a cell with a calomel reference electrode to measure standard calcium solutions with activities ranging from 0.001 M to 1.00×10^{-9} M. The following data were obtained:

Activity of Ca^{2+}, M	Cell Potential, mV
1.0×10^{-3}	93
1.0×10^{-4}	73
1.0×10^{-5}	37
1.0×10^{-6}	2
1.0×10^{-7}	−23
1.0×10^{-8}	−51
1.0×10^{-9}	−55

Plot the cell potential versus the pCa and determine the pCa value where the plot deviates significantly from linearity. For the linear portion, determine the slope and intercept of the plot. Does the plot obey the expected Equation 21-23?

(e) For Electrode 2, the following results were obtained:

Activity of Ca^{2+}	Cell Potential, V
1.0×10^{-3}	228
1.0×10^{-4}	190
1.0×10^{-5}	165
1.0×10^{-6}	139
5.6×10^{-7}	105
3.2×10^{-7}	63
1.8×10^{-7}	36
1.0×10^{-7}	23
1.0×10^{-8}	18
1.0×10^{-9}	17

Again, plot cell potential versus pCa and determine the range of linearity for Electrode 2. Determine the slope and intercept for the linear portion. Does this electrode obey Equation 21-23 for the higher Ca^{2+} activities?

(f) Electrode 2 is said to be super-Nernstian for concentrations from 10^{-7} M to 10^{-6} M. Why is this term used? If you have access to a library that subscribes to *Analytical Chemistry* or has Web access to the journal, read the article. This electrode is said to have Ca^{2+} uptake. What does this mean and how might it explain the response?

(g) Electrode 3 gave the following results:

Activity of Ca^{2+}, M	Cell Potential, mV
1.0×10^{-3}	175
1.0×10^{-4}	150
1.0×10^{-5}	123
1.0×10^{-6}	88
1.0×10^{-7}	75
1.0×10^{-8}	72
1.0×10^{-9}	71

Plot the cell potential versus pCa and determine the range of linearity. Again, determine the slope and intercept. Does this electrode obey Equation 21-23?

(h) Electrode 3 is said to have Ca^{2+} release. Explain this term from the article and describe how it might explain the response.

(i) Does the article give any alternative explanations for the experimental results? If so, describe these alternatives.

[13] A. Ceresa, E. Pretsch, and E. Bakker, *Anal. Chem.*, **2000**, *72*, 2054, **DOI**: 10.1021/ac991092h.