Analytical chemistry

Lecture № 34

Electrochemical Methods of Analysis

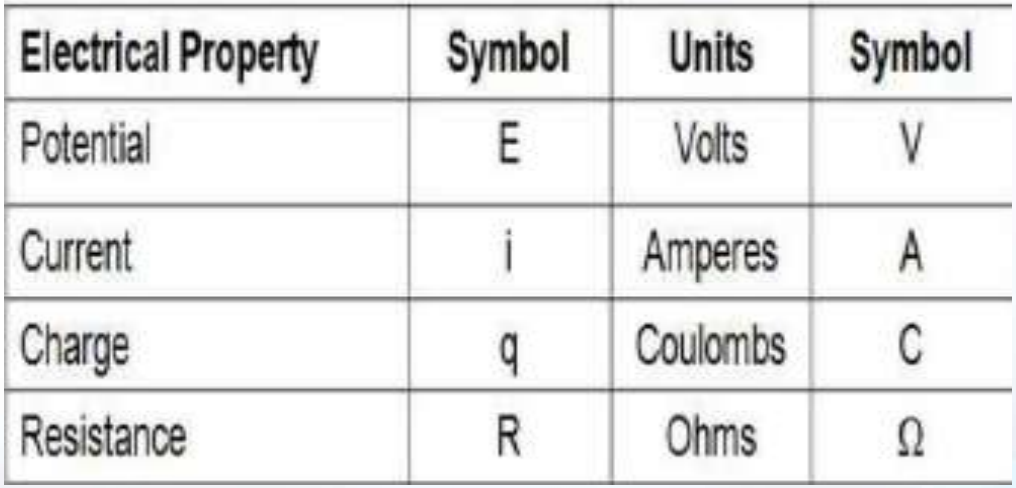
Part I

Electroanalytical techniques are concerned with the interplay between electricity & chemistry, namely the measurement of electrical quantities such as current, potential or charge and their relationship to chemical parameters such as concentration. The use of electrical measurements for analytical purposes has found large range of applications including environmental monitoring, industrial quality control & biomedical analysis.

Electroanalytical methods have certain advantages over other analytical methods. Electrochemical analysis allows for the determination of different oxidation states of an element in a solution, not just the total concentration of the element. Electroanalytical techniques are capable of producing exceptionally low detection limits and an abundance of characterization information including chemical kinetics information. The other important advantage of this method is its low cost.

Classification

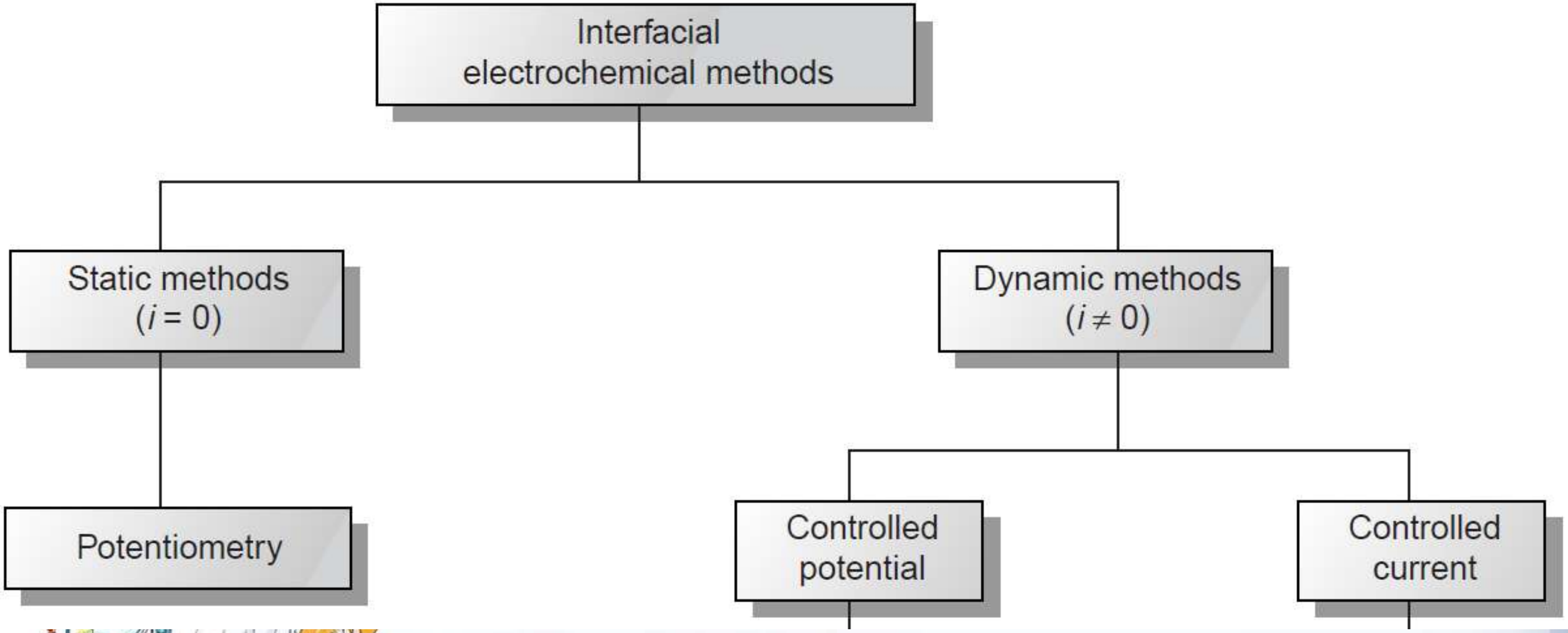
There are only three principal sources for the analytical signal—potential, current, and charge—a wide variety of experimental designs are possible. The simplest division is between ***bulk methods***, which measure properties of the whole solution, and ***interfacial methods***, in which the signal is a function of phenomena occurring at the interface between an electrode and the solution in contact with the electrode. The measurement of a solution's conductivity, which is proportional to the total concentration of dissolved ions, is one example of a bulk electrochemical method. A determination of pH using a pH electrode is one example of an interfacial electrochemical method.



Electrical Property	Symbol	Units	Symbol
Potential	E	Volts	V
Current	i	Amperes	A
Charge	q	Coulombs	C
Resistance	R	Ohms	Ω

Interfacial Electrochemical Methods

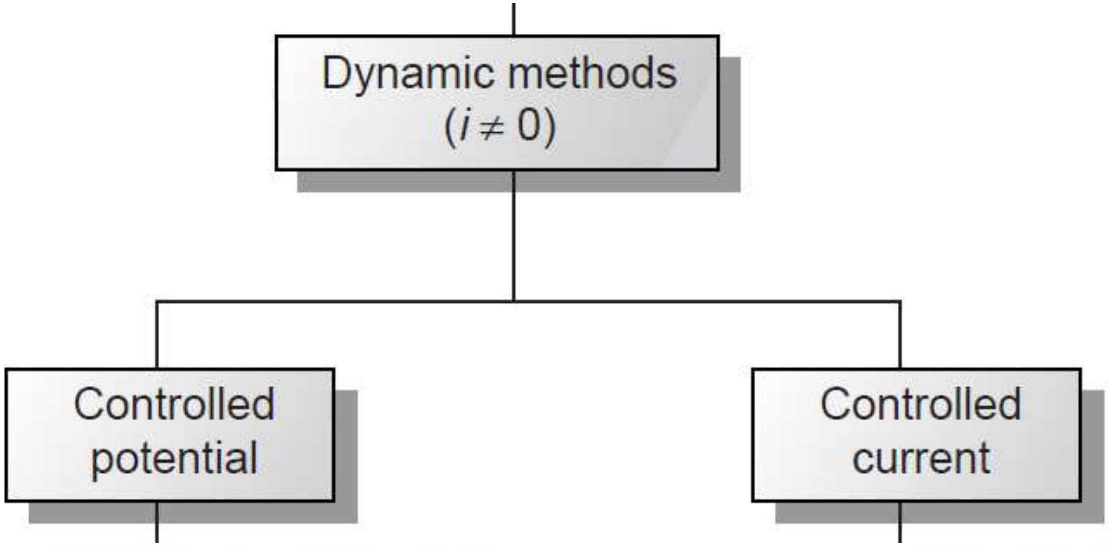
Interfacial electrochemical methods are divided into ***static methods*** and ***dynamic methods***. In static methods no current passes between the electrodes, and the concentrations of species in the electrochemical cell remain unchanged, or static. ***Potentiometry***, in which the potential of an electrochemical cell is measured under static conditions, is one of the most important quantitative electrochemical methods.

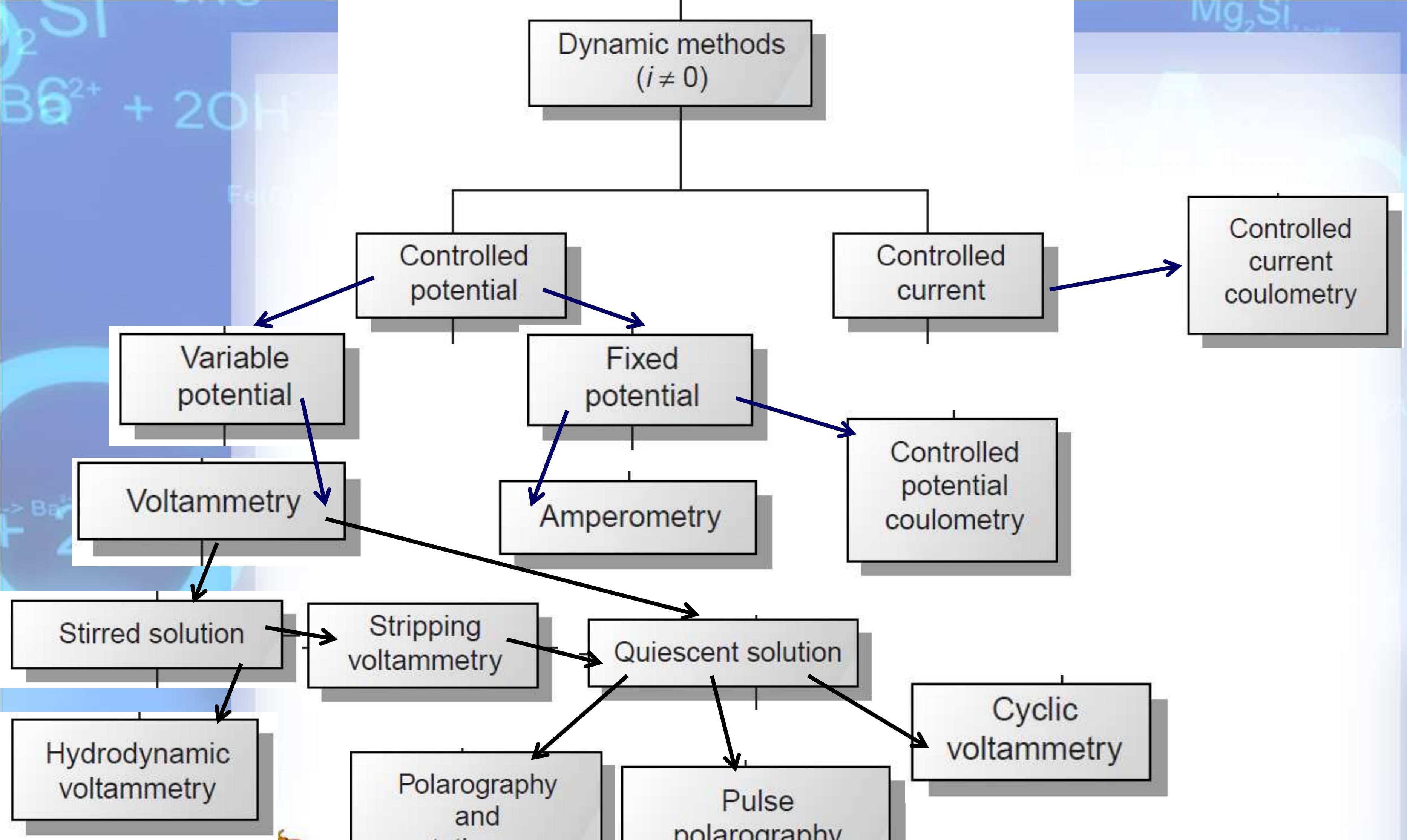


Interfacial electrochemical methods

- Static methods ($i = 0$)
  - Potentiometry
- Dynamic methods ($i \neq 0$)
  - Controlled potential
  - Controlled current

The largest division of interfacial electrochemical methods is the group of ***dynamic methods***, in which current flows and concentrations change as the result of a redox reaction. Dynamic methods are further subdivided by whether we choose to ***control the current*** or the ***potential***. In *controlled-current coulometry*, we completely oxidize or reduce the analyte by passing a fixed current through the analytical solution. *Controlled-potential methods* are subdivided further into controlled-potential ***coulometry*** and ***amperometry***, in which a constant potential is applied during the analysis, and voltammetry, in which the potential is systematically varied.





Dynamic methods ($i \neq 0$)

Controlled potential

Controlled current

Controlled current coulometry

Variable potential

Fixed potential

Voltammetry

Amperometry

Controlled potential coulometry

Stirred solution

Stripping voltammetry

Quiescent solution

Hydrodynamic voltammetry

Polarography and stationary electrode voltammetry

Pulse polarography and voltammetry

Cyclic voltammetry

Electrochemical measurements are made in an electrochemical cell, consisting of two or more electrodes and associated electronics for controlling and measuring the current and potential.

The simplest electrochemical cell uses two electrodes. The potential of one of the electrodes is sensitive to the analyte’s concentration and is called the working, or ***indicator electrode*****.** The second electrode, which is called the ***counter electrode*****,** serves to complete the electric circuit and provides a reference potential against which the working electrode’s potential is measured. Ideally the counter electrode’s potential remains constant so that any change in the overall cell potential is attributed to the working electrode. In a dynamic method, where the passage of current changes the concentration of species in the electrochemical cell, the potential of the counter electrode may change over time. This problem is eliminated by replacing the counter electrode with two electrodes: a ***reference electrode*****,** through which no current flows and whose potential remains constant; and an ***auxiliary electrode*** that completes the electric circuit and through which current is allowed to flow.

Electrochemical Cells

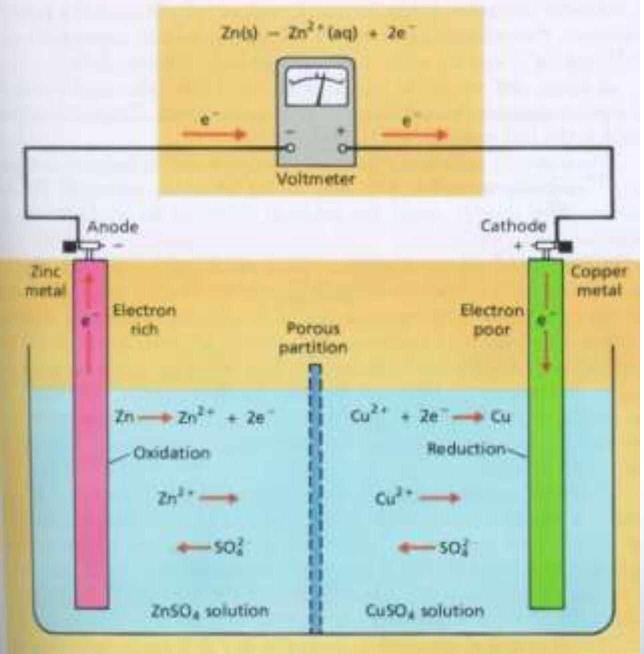
- Cathode is electrode at which reduction occurs.
- Anode is electrode at which oxidation occurs.
- Indicator and Reference electrodes
- Junction potential is small potential at the interface between two electrolytic solutions that differ in composition.

Galvanic and Electrolytic Cells

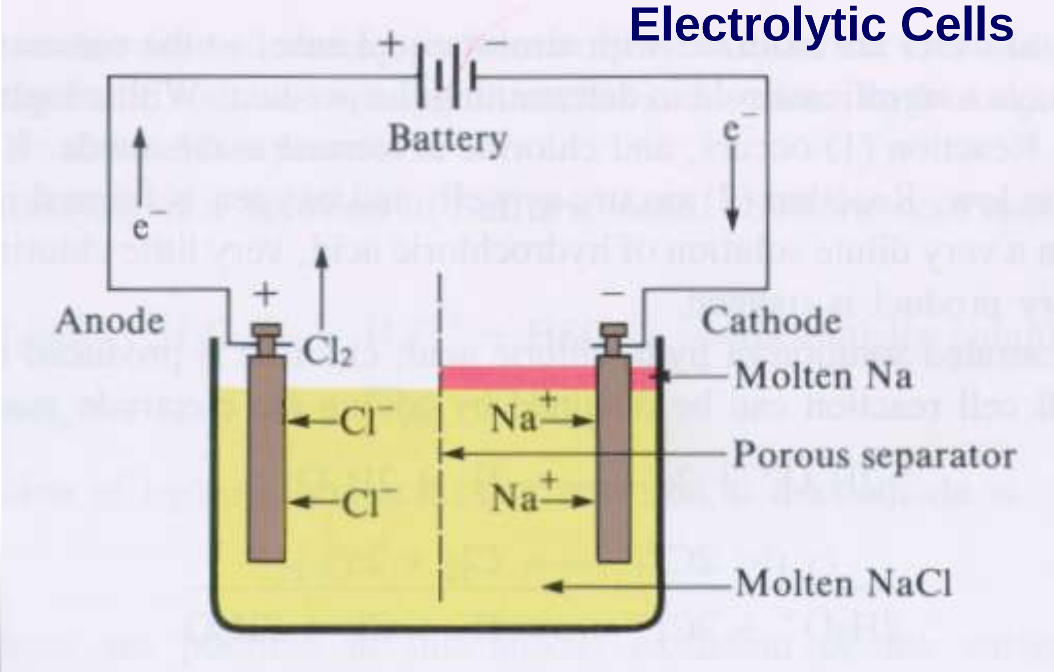
- Galvanic cells produce electrical energy.
- Electrolytic cells consume energy.

– If the cell is a chemically reversible cell, then it can be made electrolytic by connecting the negative terminal of a DC power supply to the zinc electrode and the positive terminal to the copper electrode.

Galvanic Cells



Electrolytic Cells



Although many different electrochemical methods of analysis are possible, there are only three basic experimental designs:

(1) measuring the potential under static conditions of no current flow;

(2) measuring the potential while controlling the current; and

(3) measuring the current while controlling the potential.

Each of these experimental designs, however, is based on **Ohm's law** that a current, *I,* passing through an electric circuit of resistance, *R, generates a potential, E;*

$$E = iR$$

Measuring the potential of an electrochemical cell under conditions of zero current is accomplished using a ***potentiometer*.**

The current in the upper half of the circuit is

$$i_{\mathrm{up}} = \frac{E_{\mathrm{PS}}}{R_{ab}}$$

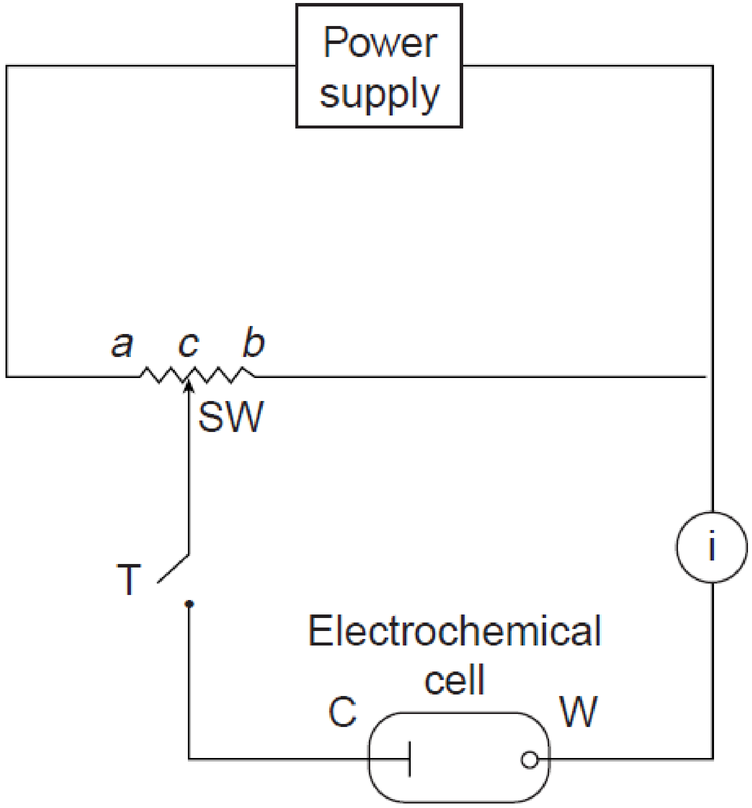
where E_{PS} is the power supply’s potential, and R_{ab} is the resistance between points a and b of the slide-wire resistor. In a similar manner, the current in the lower half of the circuit is

$$i_{\mathrm{low}} = \frac{E_{\mathrm{cell}}}{R_{\mathrm{cb}}}$$

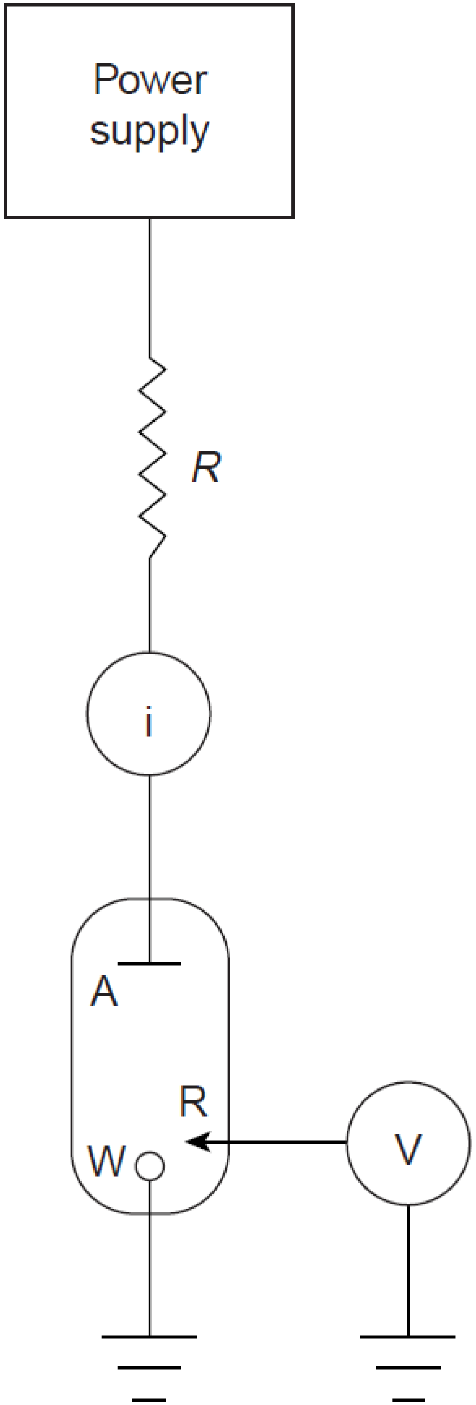
where E_{cell} is the potential difference between the working electrode and the counter electrode, and R_{cb} is the resistance between the points c and b of the slide-wire resistor. When $i_{up} = i_{low} = 0$ no current flows through the galvanometer and the cell potential is given by

$$E_{\mathrm{cell}} = \frac{R_{cb}}{R_{ab}} \times E_{\mathrm{PS}}$$

To make a measurement the tap key is pressed momentarily, and the current is noted at the galvanometer. If a nonzero current is registered, then the slide wire is adjusted and the current remeasured. This process is continued until the galvanometer registers a current of zero.



Schematic diagram of a manual potentiostat: C = counter electrode; W = working electrode; SW = slide-wire resistor; T = tap key; i = galvanometer.



A ***galvanostat*** is used for dynamic methods, such as constant-current coulometry, in which it is necessary to control the current flowing through an electrochemical cell.

If the resistance, *R,* of the galvanostat is significantly larger than the resistance of the electrochemical cell, and the applied voltage from the power supply is much greater than the cell potential, then the current between the auxiliary and working electrodes is equal to

$$i = \frac{E_{PS}}{R}$$

The potential of the working electrode, which changes as the composition of the electrochemical cell changes, is monitored by including a reference electrode and a high-impedance potentiometer.

Schematic diagram of a galvanostat:
R = resistor; i = galvanometer; A = auxiliary
electrode; W = working electrode;
R = reference electrode; V = voltmeter or
potentiometer (optional).

Potentiometry

In potentiometry the potential of an electrochemical cell is measured under static conditions. Because no current, or only a negligible current, flows while measuring a solution's potential, its composition remains unchanged. For this reason, potentiometry is a useful quantitative method. The first quantitative potentiometric applications appeared soon after the formulation, in 1889, of the Nernst equation relating an electrochemical cell's potential to the concentration of electroactive species in the cell.

When first developed, potentiometry was restricted to redox equilibria at metallic electrodes, limiting its application to a few ions. In 1906, Cremer discovered that a potential difference exists between the two sides of a thin glass membrane when opposite sides of the membrane are in contact with solutions containing different concentrations of H_3O^+. This discovery led to the development of the glass pH electrode in 1909. Other types of membranes also yield useful potentials. Kolthoff and Sanders, for example, showed in 1937 that pellets made from AgCl could be used to determine the concentration of Ag^+. Electrodes based on membrane potentials are called ion-selective electrodes, and their continued development has extended potentiometry to a diverse array of analytes.

GENERAL PRINCIPLES

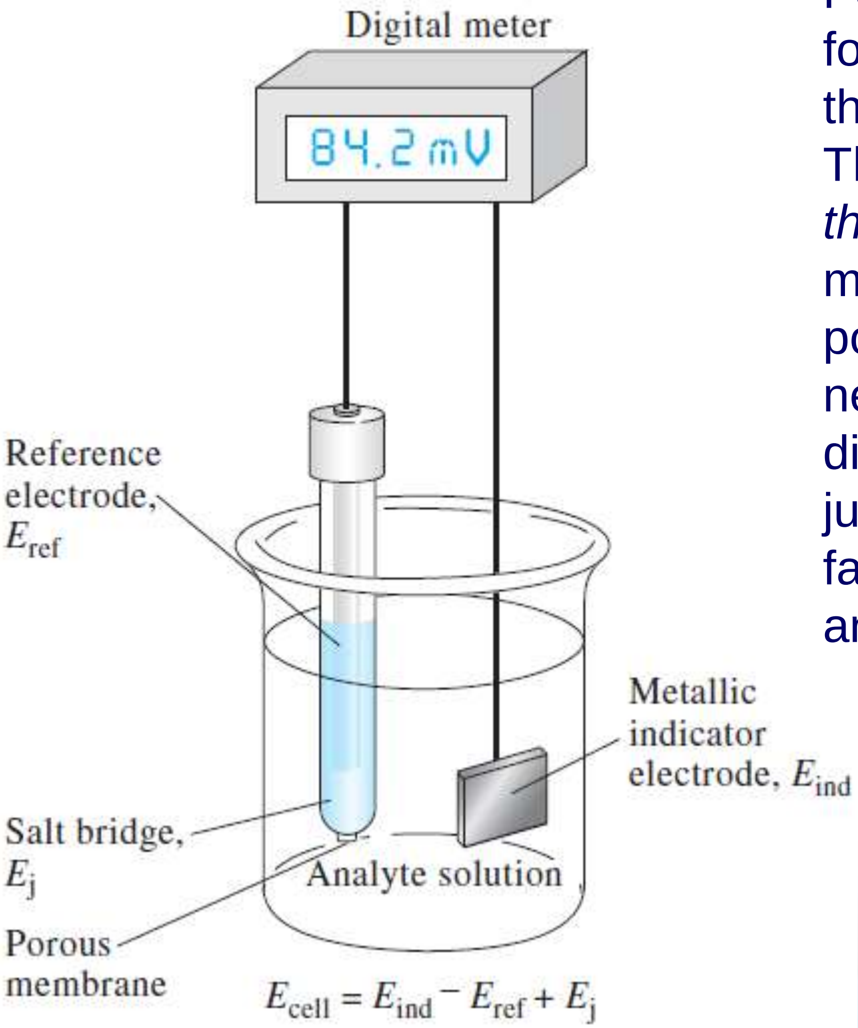
Absolute values for individual half-cell potentials cannot be determined in the laboratory, that is, only relative cell potentials can be measured experimentally. This cell can be represented as

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

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 lefthand 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.

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.

A cell for potentiometric determinations



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, *Ej, 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.

By convention, the reference electrode is taken to be the anode;

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

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.

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.

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:

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

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

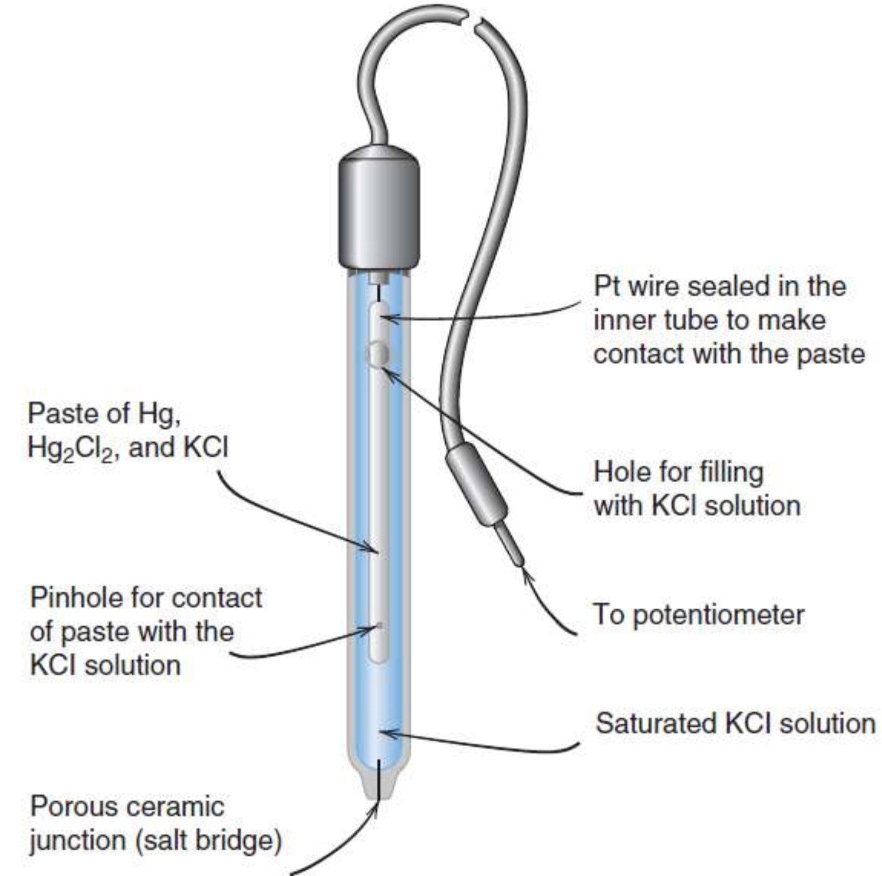
$$\mathrm{Hg_2Cl_2}(s) + 2e^- \rightleftharpoons 2\mathrm{Hg}(l) + 2\mathrm{Cl^-}(aq)$$

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

The Nernst equation for the calomel electrode is

$$E = E^{\circ}_{Hg_2Cl_2/Hg} - \frac{0.05916}{2}\log[Cl^-]^2 = +0.2682 - \frac{0.05916}{2}\log[Cl^-]^2$$

The potential of a calomel electrode, therefore, is determined by the concentration of Cl^-. The ***saturated calomel electrode (SCE),*** which is constructed using an aqueous solution saturated with KCl, has a potential at 25 °C of +**0.2444** V.



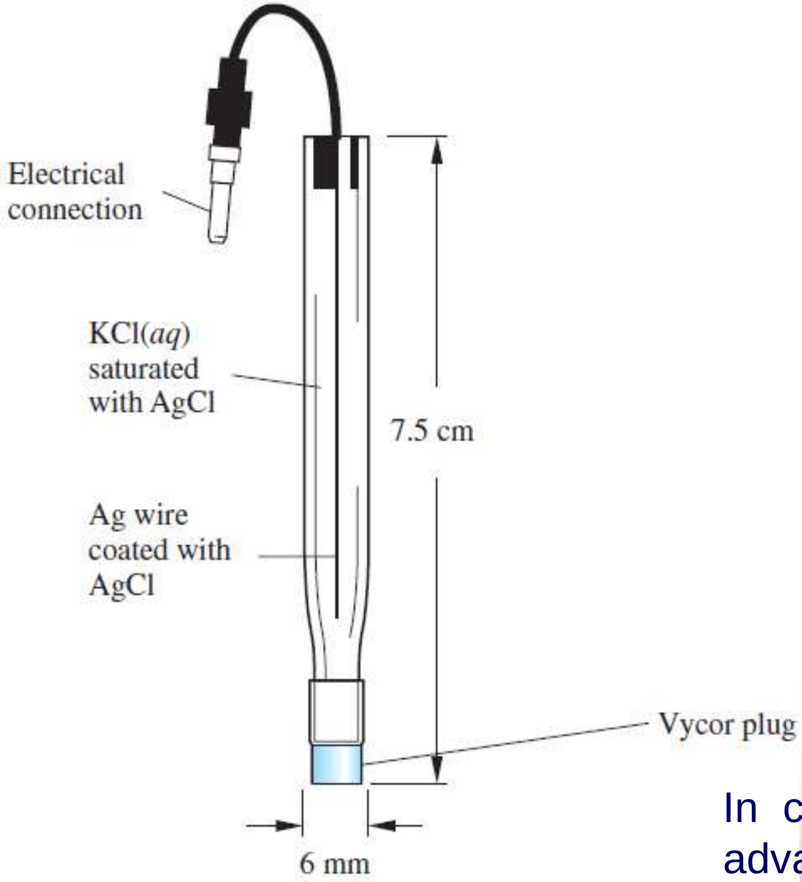
A typical SCE consists of an inner tube, packed with a paste of Hg, Hg_2Cl_2, and saturated KCl, situated within a second tube filled with a saturated solution of KCl. A small hole connects the two tubes, and an asbestos fiber serves as a salt bridge to the solution in which the SCE is immersed. The stopper in the outer tube may be removed when additional saturated KCl is needed.

Silver/Silver Chloride Electrodes

Another common reference electrode is the ***silver/silver chloride electrode*****,** which is based on the redox couple between AgCl and Ag.

$$\mathrm{AgCl}(s) + e^- \rightleftharpoons \mathrm{Ag}(s) + \mathrm{Cl}^- \qquad \mathrm{Ag}|\mathrm{AgCl}(\mathrm{sat'd}),\ \mathrm{KCl}(\mathrm{sat'd})||$$

As with the saturated calomel electrode, the potential of the Ag/AgCl electrode is determined by the concentration of Cl– used in its preparation.



When prepared using a saturated solution of KCl, the Ag/AgCl electrode has a potential of +**0.197** V at 25 °C. Another common Ag/AgCl electrode uses a solution of 3.5 M KCl and has a potential of **+0.205** at 25 °C. The Ag/AgCl electrode prepared with saturated KCl, of course, is more temperature-sensitive than one prepared with an unsaturated solution of KCl. A typical Ag/AgCl electrode consists of a silver wire, the end of which is coated with a thin film of AgCl. The wire is immersed in a solution that contains the desired concentration of KCl and that is saturated with AgCl. A porous plug serves as the salt bridge.

In comparison to the SCE the Ag/AgCl electrode has the advantage of being useful at higher temperatures

Indicator Electrodes

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***.

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

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

the potential of the electrode is determined by the concentration of copper ion.

$$E = E^{\circ}_{Cu^{2+}/Cu} - \frac{0.05916}{2}\log\frac{1}{[Cu^{2+}]} = +0.3419 - \frac{0.05916}{2}\log\frac{1}{[Cu^{2+}]}$$

Metallic indicator electrodes in which a metal is in contact with a solution containing its ion are called **electrodes of the first kind.** In general, for a metal M, in a solution of M^{n+}, *the cell potential is given as*

$$E_{\text{cell}} = K - \frac{0.05916}{n}\log\frac{1}{[\mathrm{M}^{n+}]} = K + \frac{0.05916}{n}\log[\mathrm{M}^{n+}]$$

where *K is a constant that includes the standard-state potential for the* M^{n+}/M redox couple, the potential of the reference electrode, and the junction potential. For a variety of reasons, including slow kinetics for electron transfer, the existence of surface oxides and interfering reactions, electrodes of the first kind are limited to Ag, Bi, Cd, Cu, Hg, Pb, Sn, Tl, and Zn. Many of these electrodes, such as Zn, cannot be used in acidic solutions where they are easily oxidized by H^+.

Electrodes of the Second Kind

When the potential of an electrode of the first kind responds to the potential of another ion that is in equilibrium with M*n*+, *it is called an* ***electrode of the second*** **kind.** Two common electrodes of the second kind are the calomel and silver/silver chloride reference electrodes. Electrodes of the second kind also can be based on complexation reactions. For example, an electrode for EDTA is constructed by coupling a Hg^{2+}/Hg electrode of the first kind to EDTA by taking advantage of its formation of a stable complex with Hg^{2+}.

Redox Electrodes

Electrodes of the first and second kind develop a potential as the result of a redox reaction in which the metallic electrode undergoes a change in its oxidation state. Metallic electrodes also can serve simply as a source of, or a sink for, electrons in other redox reactions. Such electrodes are called **redox electrodes.** The Pt cathode is an example of a redox electrode because its potential is determined by the concentrations of Fe^{2+} and Fe^{3+} in the indicator half-cell. Note that the potential of a redox electrode generally responds to the concentration of more than one ion, limiting their usefulness for direct potentiometry.

Membrane Electrodes

The discovery, in 1906, that a thin glass membrane develops a potential, called a ***membrane potential*****,** when opposite sides of the membrane are in contact with solutions of different pH led to the eventual development of a whole new class of indicator electrodes called ionselective electrodes (ISEs). Following the discovery of the glass pH electrode, ***ionselective electrodes*** have been developed for a wide range of ions. Membrane electrodes also have been developed that respond to the concentration of molecular analytes by using a chemical reaction to generate an ion that can be monitored with an ion-selective electrode. The development of new membrane electrodes continues to be an active area of research.

Membrane Indicator Electrodes (or Ion-Selective Electrodes)

The underlying principle of this type of electrode is that the potential developed due to an unequal charge generated at the opposing surfaces of a ‘special’ membrane. The resulting charge at each surface of the membrane is exclusively controlled and monitored by the exact position of an equilibrium involving analyte ions, which in turn, solely depends upon the concentration of those ions present in the solution. Ionselective electrodes occupy a very important place in the analytical chemistry by virtue of the fact that one may use the acquired skill, expertise and wisdom to design and commercially prepare membranes that are practically selective towards a specific ion besides producing potentials according to the Nernst-type equation.

These are classified further into the following *four kinds, namely :*

- ***Glass membrane electrodes,***
- ***Polymer (liquid) membrane electrodes,***
- ***Crystalline membrane electrodes, and***
- ***Gas-sensing electrodes***

Ion-selective electrodes, such as the glass pH electrode, function by using a membrane that reacts selectively with a single ion.

$$\mathrm{Ref(samp)}\ \|\ [\mathrm{A}]_{\mathrm{samp}}\ |\ [\mathrm{A}]_{\mathrm{int}}\ \|\ \mathrm{Ref(int)}$$

where the membrane is represented by the vertical slash (|) separating the two solutionsm containing analyte. Two reference electrodes are used; one positioned within the internal solution, and one in the sample solution.

$$E_{\mathrm{cell}} = E_{\mathrm{Ref(int)}} - E_{\mathrm{Ref(samp)}} + E_{\mathrm{mem}} + E_{\mathrm{lj}}$$

where E_{mem} *is the potential across the membrane. Since the liquid junction potential* and reference electrode potentials are constant, any change in the cell’s potential is attributed to the membrane potential.

Interaction of the analyte with the membrane results in a membrane potential if there is a difference in the analyte’s concentration on opposite sides of the membrane. One side of the membrane is in contact with an internal solution containing a fixed concentration of analyte, while the other side of the membrane is in contact with the sample. Current is carried through the membrane by the movement of either the analyte or an ion already present in the membrane’s matrix.

The membrane potential is given by a Nernst-like equation

$$E_{\text{cell}} = K + \frac{0.05916}{z} \log [\text{A}]_{\text{samp}}$$

where *K is a constant accounting for the potentials of the reference electrodes, any* liquid junction potentials, the asymmetry potential, and the concentration of analyte in the internal solution.

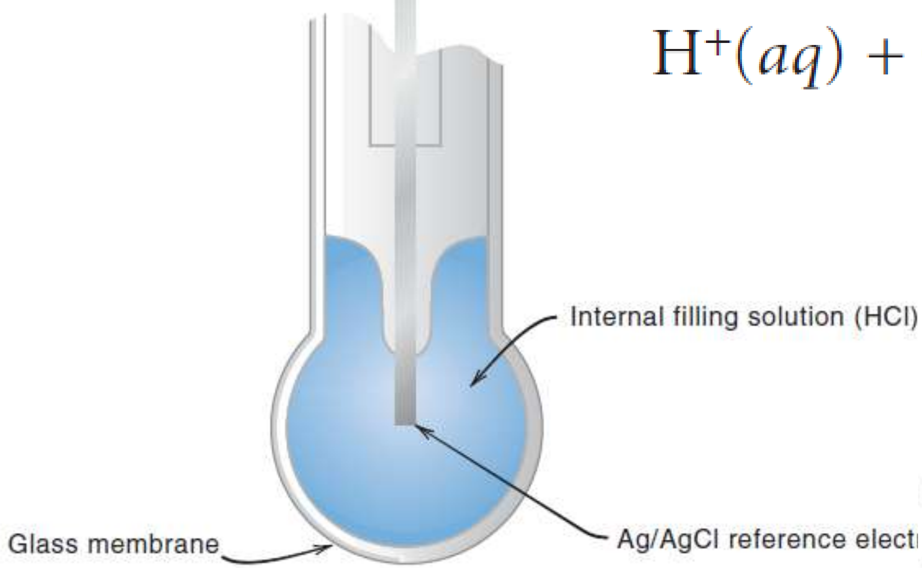
Selectivity of Membranes

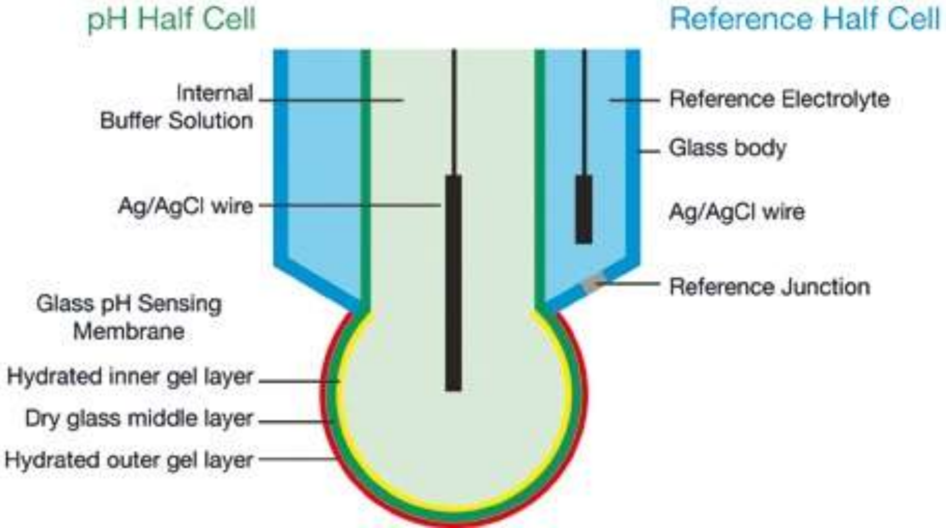
Membrane potentials result from a chemical interaction between the analyte and active sites on the membrane’s surface. Because the signal depends on a chemical process, most membranes are not selective toward a single analyte. Instead, the membrane potential is proportional to the concentration of all ions in the sample solution capable of interacting at the membrane’s active sites.

Glass Ion-Selective Electrodes

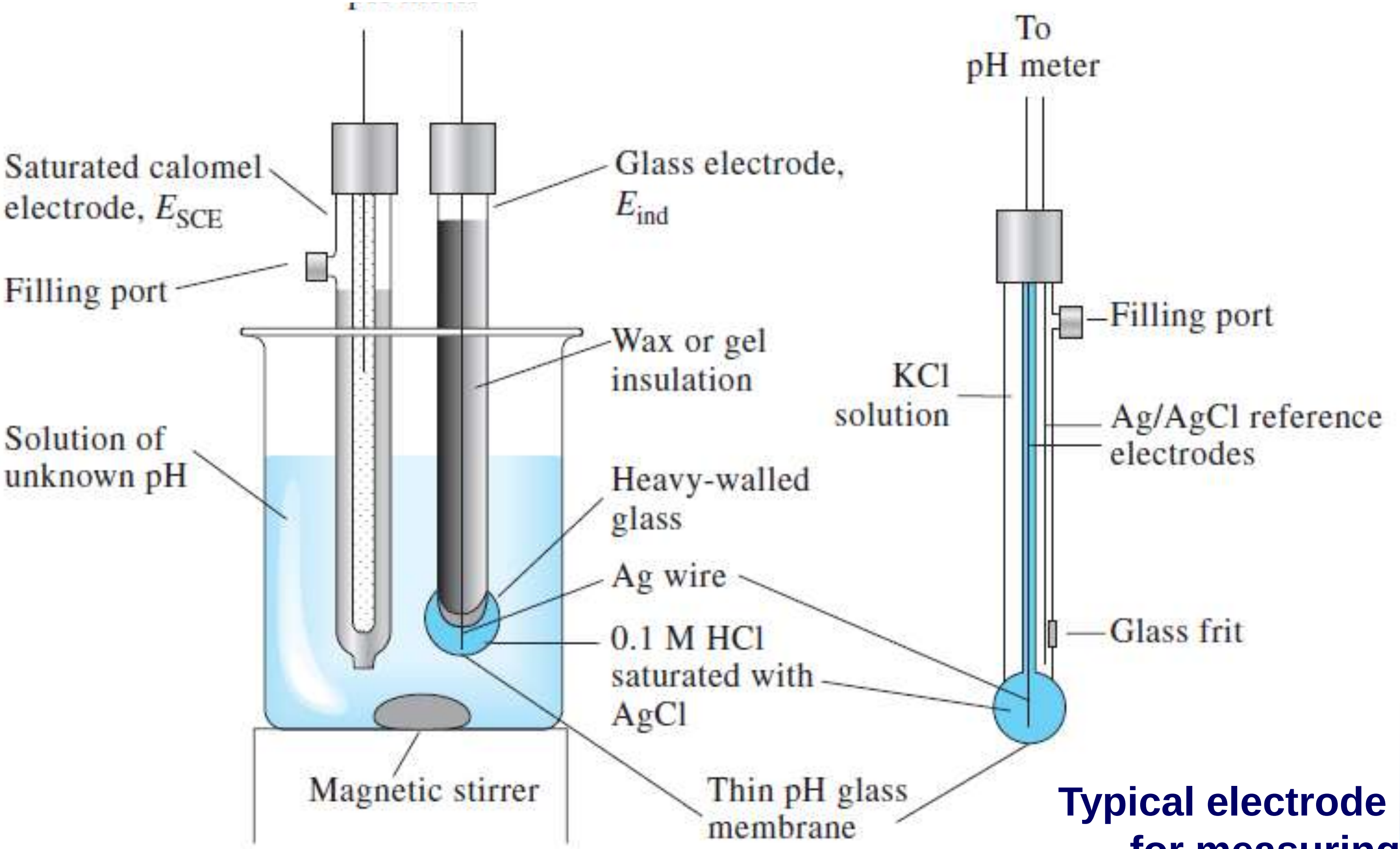
The first commercial ***glass electrodes*** were manufactured using Corning 015, a glass with a composition of approximately 22% Na_2O, 6% CaO, and 72% SiO_2. When immersed in an aqueous solution, the outer approximately 10 nm of the membrane becomes hydrated over the course of several hours. Hydration of the glass membrane results in the formation of negatively charged sites, G^-, that are part of the glass membrane's silica framework. Sodium ions, which are able to move through the hydrated layer, serve as the counterions. Hydrogen ions from solution diffuse into the membrane and, since they bind more strongly to the glass than does Na^+, displace the sodium ions giving rise to the membrane's selectivity for H+. The transport of charge across the membrane is carried by the Na^+ ions.

$$H^+(aq) + G^-\text{–}Na^+(s) \rightleftharpoons G^-\text{–}H^+(s) + Na^+(aq)$$





(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.

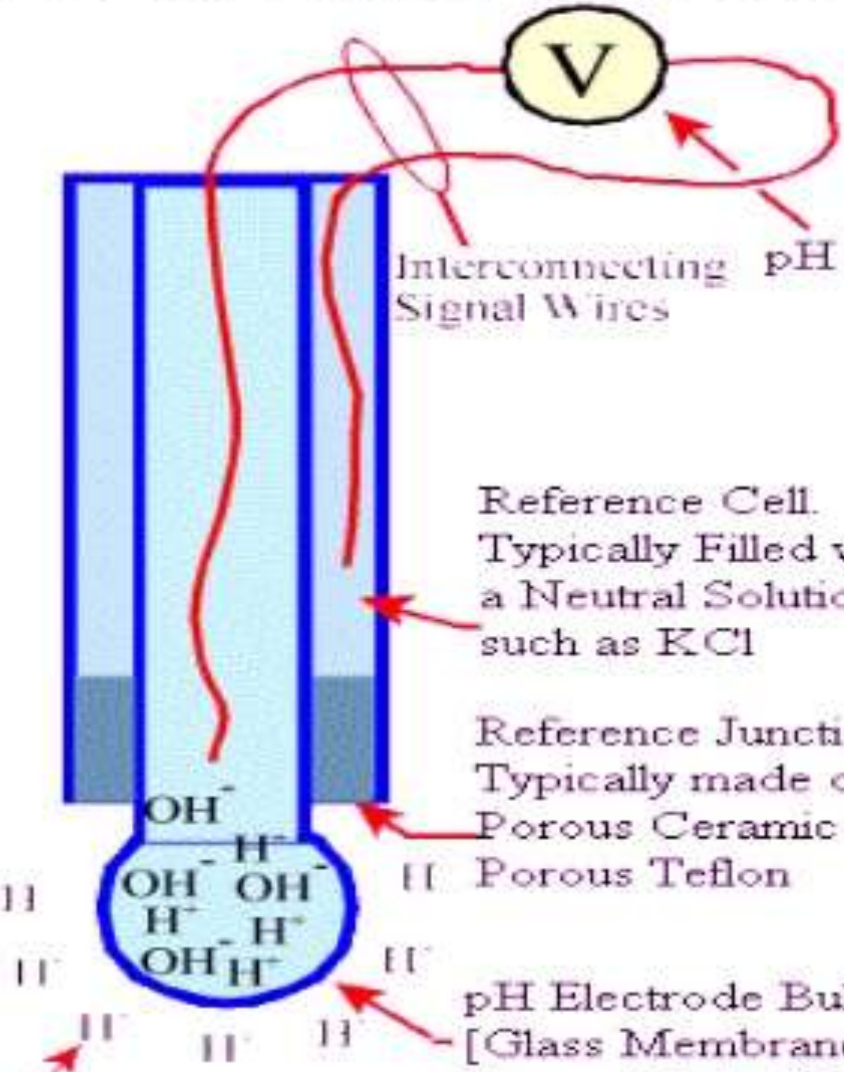


Typical electrode system for measuring pH

Construction of pH Glass Electrode

Ag/AgCl reference electrode

Glass pH electrode



Interconnecting Signal Wires

pH Meter

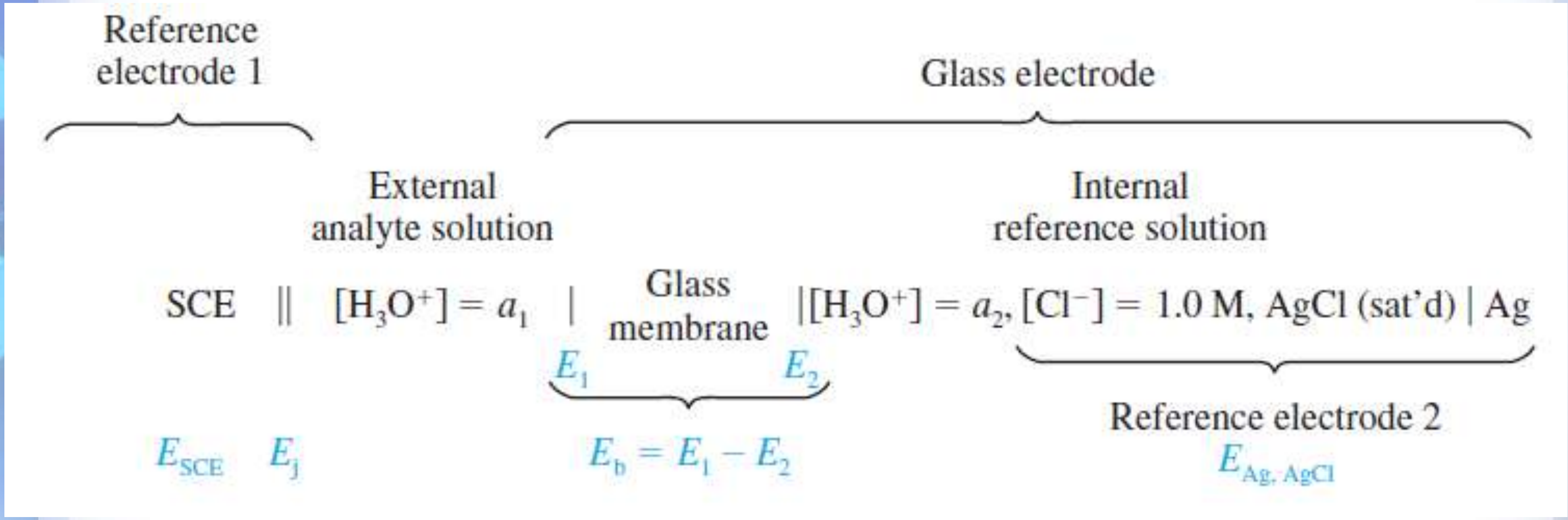
Reference Cell. Typically Filled with a Neutral Solution such as KCl

Reference Junction. Typically made of Porous Ceramic or Porous Teflon

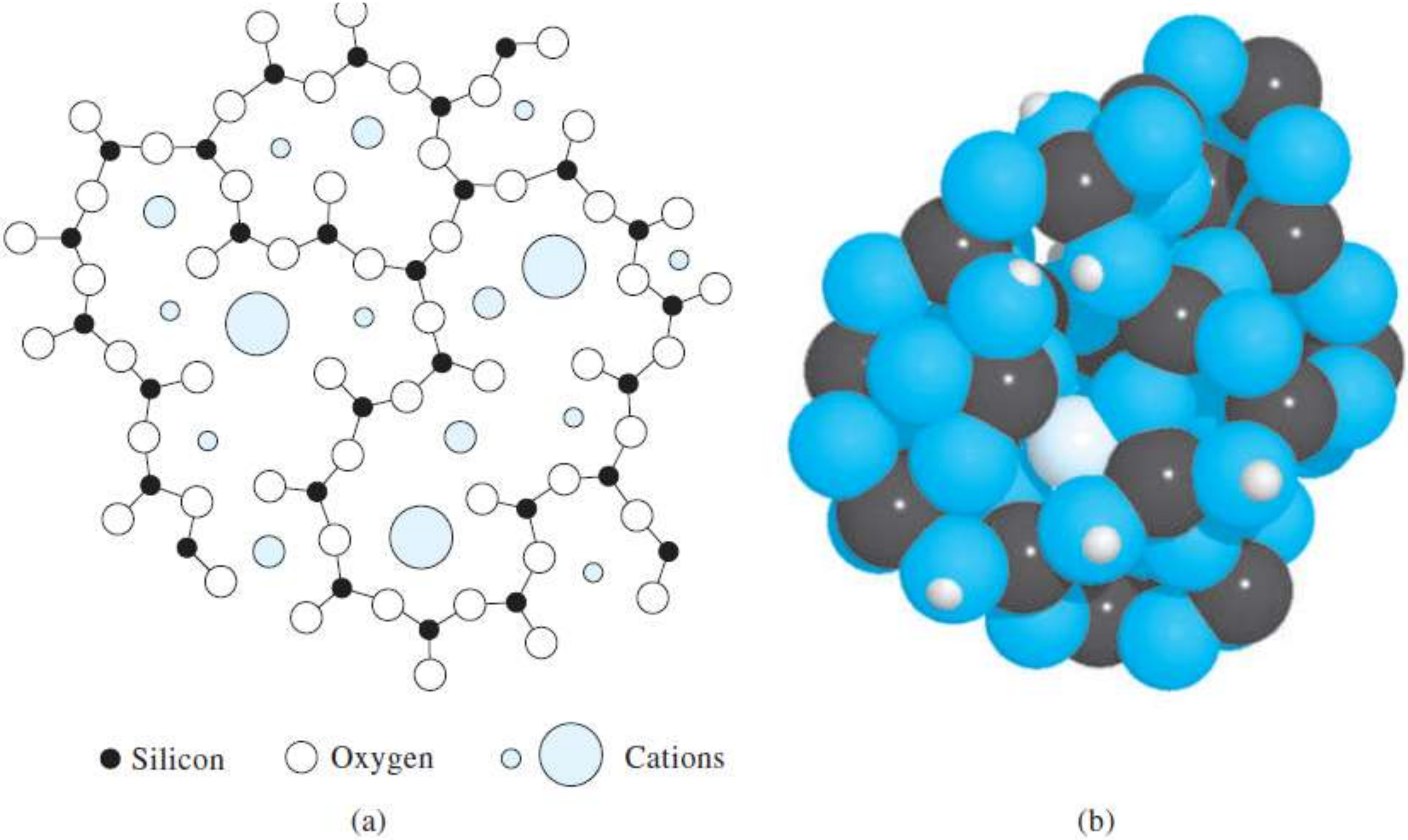
pH Electrode Bulb. [Glass Membrane that is Permeable by H+ ions.]

Probe shown in an acidic environment which has an excess of H+ ions.

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.



(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. (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 response of the Corning 015 glass membrane to monovalent cations other than H^+ at high pH led to the development of glass membranes possessing a greater selectivity for other cations. For example, a glass membrane with a composition of 11% Na_2O, 18% Al_2O_3, and 71% SiO_2 is used as a Na^+ ion-selective electrode. Other glass electrodes have been developed for the analysis of Li^+, K^+, Rb^+, Cs^+, NH_4^+, Ag^+, and Tl^+. Since the typical thickness of the glass membrane in an ion-selective electrode is about 50 mm, they must be handled carefully to prevent the formation of cracks or breakage. Before a glass electrode can be used it must be conditioned by soaking for several hours in a solution containing the analyte. Glass electrodes should not be allowed to dry out, as this destroys the membrane's hydrated layer. If a glass electrode has been allowed to dry out, it must be reconditioned before it can be used. The composition of a glass membrane changes over time, affecting the electrode's performance. The average lifetime for a glass electrode is several years.

THE pH METER

We create a voltaic cell with the indicator and reference electrodes. We measure the voltage of the cell, giving a reading of the indicator electrode potential relative to the reference electrode. We can relate this to the analyte activity or concentration using the Nernst equation.

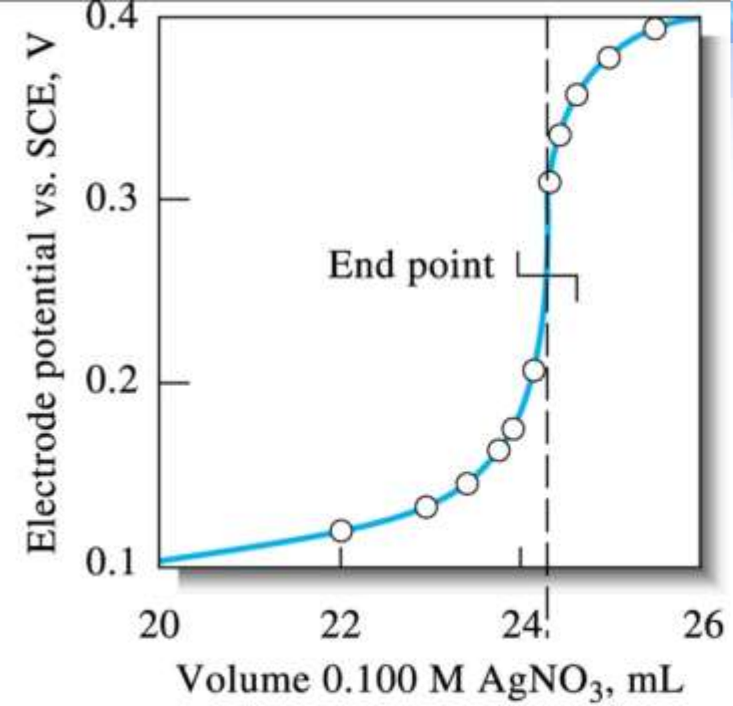
A pH meter is a high-input impedance ***voltmeter*** that senses the cell voltage, provides a digital readout (either in terms of voltage or pH) and often provides an amplified output to be acquired by an external data system device.

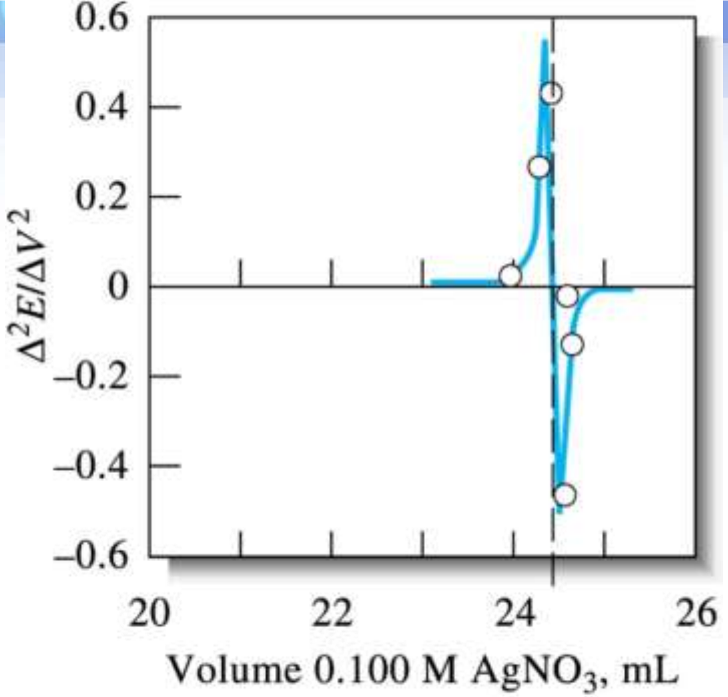
Because very little current is drawn, chemical equilibrium is not perceptibly disturbed. This is vital for monitoring irreversible reactions that do not return to the prior state if an appreciable amount of current is drawn. The resistance of a typical glass pH electrode is of the order of 10^8 Ω.

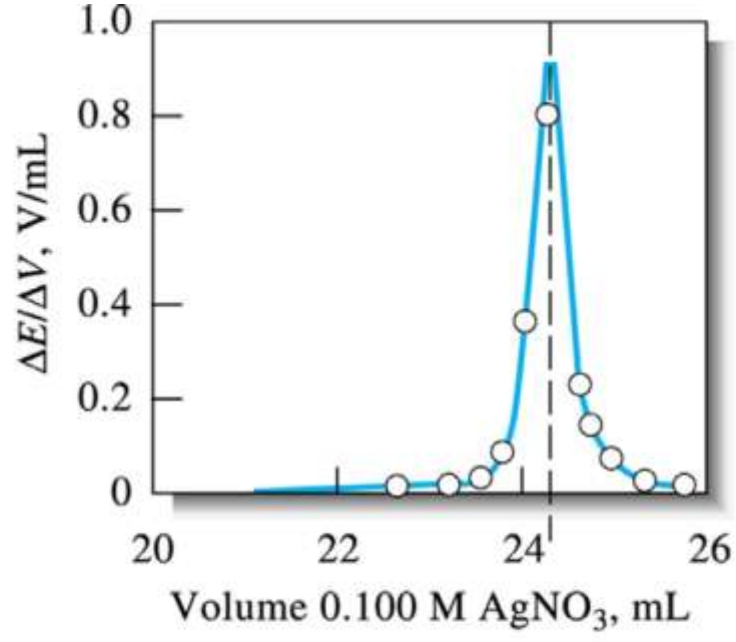
In a **potentiometric titration,** we measure the potential of a suitable indicator electrode as a function of titrant volume. The information provided by a potentiometric titration is different from the data obtained in a direct potentiometric measurement. For example, the direct measurement of 0.100 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.

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. 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 as a function of the average volume *V produces a curve with a maximum* that corresponds to the point of inflection.

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.







Potentiometric Titration Curves (*a*) *Sigmoid (Regular) Curve ; (b) First Derivative Curve ; (c) Second Derivative Curve.*

Figure (*a*) *gives rise to a* ***sigmoid-curve (or S-shaped curve)*** obtained either by using an appropriate equipment (automatic titrators) that plots the graph automatically* as the titration proceeds, or manually by plotting the raw experimental data. Figure (*b*) *is obtained by plotting $\Delta E/\Delta V$ against V which is termed as the* ***first derivative*** **curve.** It gives a maximum at the point of inflexion of the titration curve i.e., at the end-point. Figure (*c*) *is known as the* ***second derivative curve.*** Thus, the second derivative becomes zero at the point of inflexion and hence, affords a more exact measurement of the equivalence point.

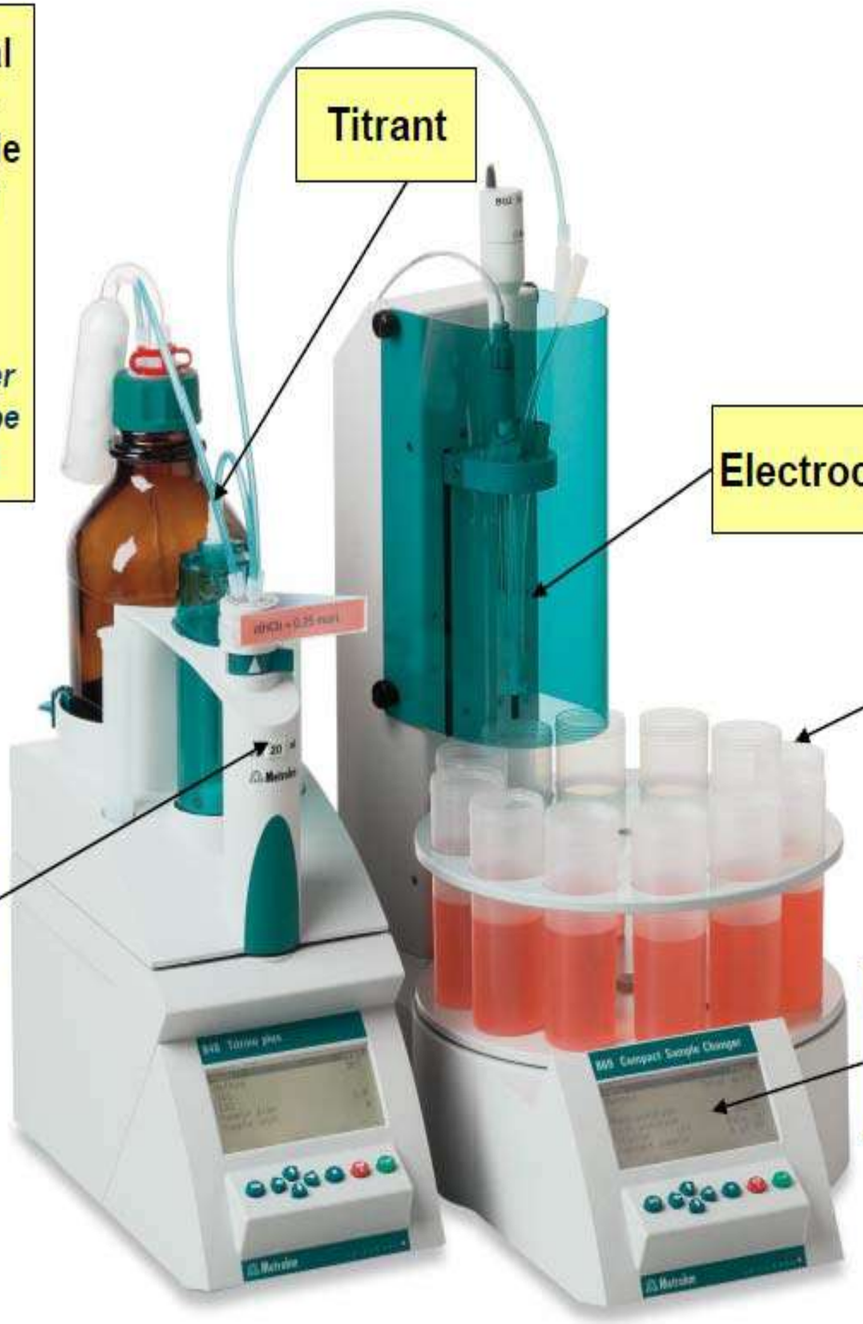
Advantages of potentiometric over visual indicators

There are number of advantages offered by potentiometric indicators over visual indicators to follow the progress of titrimetric reactions and detect end-points. These are:

- Ability to function is highly coloured solutions;
- Ability to find multiple end-points when samples contain more than one titratable species. For instance, a sample containing both weak and strong acids or polyprotic acids (eg: orthophosphoric acid H_3PO_4) where there is a significant difference between the K_a values of the titratable protons. **See example (9.i) on the next slide**
- Offers opportunities for automation for both detection of end-points and for the analysis of multiple samples dispensed from auto-samplers.

Figure 4.12 shows a typical automatic potentiometric titration instrument, capable of allowing 12 samples of the same type to be analysed sequentially.

The image is displayed by permission of Metrohm. Further details of this equipment may be found at www.metrohm.com



Titrant

Electrochemical cell

Titration vessels

Auto burette

Computer electronics and read-out display

Figure 9.23 - typical potentiometric auto-titrator

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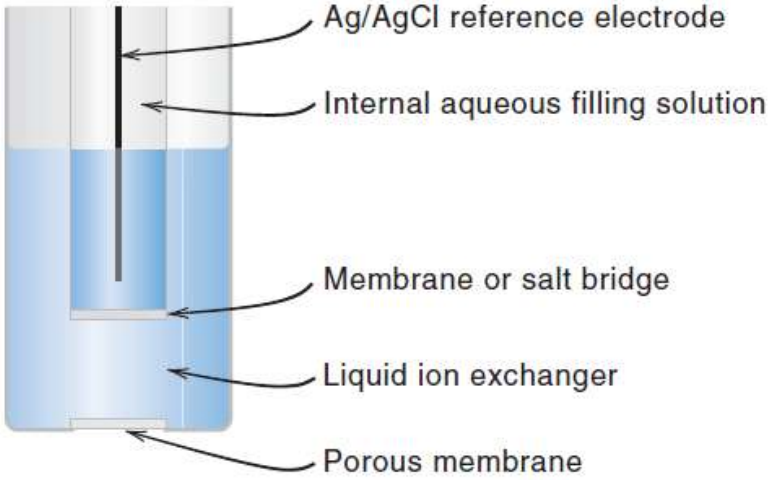
The analysis of intercellular fluids requires an ion-selective electrode that can be inserted directly into the desired cell. Liquid-based membrane **microelectrodes** with tip diameters of less than 1 mm are constructed by heating and drawing out a hard-glass capillary tube with an initial diameter of approximately 1–2 mm. The tip of the microelectrode is made hydrophobic by dipping in dichlorodimethyl silane. An inner solution appropriate for the desired analyte and a Ag/AgCl wire reference electrode are placed within the microelectrode. The tip of the microelectrode is then dipped into a solution containing the liquid complexing agent. The small volume of liquid complexing agent entering the microelectrode is retained within the tip by capillary action, eliminating the need for a solid membrane. Potentiometric microelectrodes have een developed for a number of clinically important analytes, including H^+, K^+, Na^+, Ca^{2+}, Cl^-, and I^-.

Photograph of a potassium liquid ion exchanger microelectrode with 125 mm of ion exchanger inside the tip. The magnification of the original photo was 400.

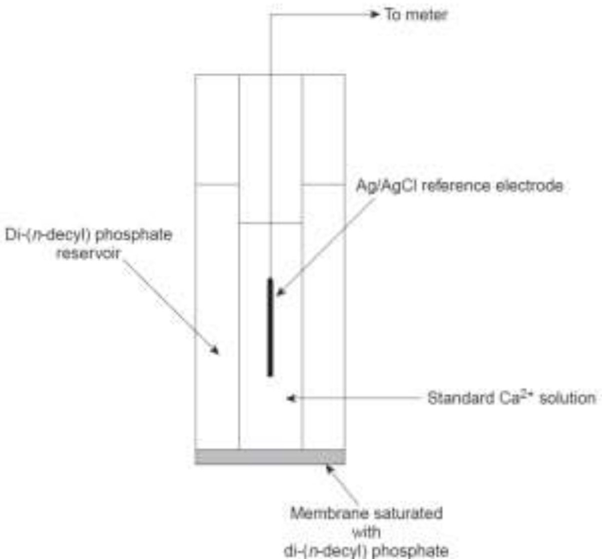
Liquid-Based Ion-Selective Electrodes

Another approach to constructing an ion-selective electrode is to use a hydrophobic membrane containing a selective, liquid organic complexing agent. Three types of organic liquids have been used: cation exchangers, anion exchangers, and neutral **ionophores.** When the analyte's concentration on the two sides of the membrane is different, a membrane potential is the result. Current is carried through the membrane by the analyte. One example of a liquid-based ion-selective electrode is that for Ca^{2+}, which uses a porous plastic membrane saturated with di-(*n-decyl) phosphate.* the membrane is placed at the end of a nonconducting cylindrical tube and is in contact with two reservoirs. The outer reservoir contains di-(*n-decyl) phosphate in di-n-octylphenylphosphonate, which soaks into* the porous membrane. The inner reservoir contains a standard aqueous solution of Ca^{2+} and a Ag/AgCl reference electrode.



$(C_{10}H_{21}O)_2PO_2^-$

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

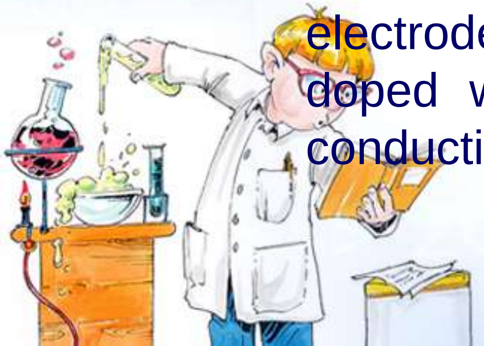


The active membrane generally contains the ion of interest selectively bound to a reagent in the membrane, either as a precipitate or a complex. Otherwise, the electrode must be equilibrated in a solution of the test ion, in which case the ion also binds selectively to the membrane reagent. The secret in constructing ion-selective electrodes, then, is to find a material that has sites which show strong affinity for the ion of interest. Thus, the calcium liquid ion exchange electrode exhibits high selectivity for calcium over magnesium and sodium ions because the organophosphate cation exchanger has a high chemical affinity for calcium ions. The ion exchange equilibrium at the membrane–solution interface involves calcium ions, and the potential depends on the ratio of the activity of calcium ions in the external solution to that of calcium ion in the membrane phase.

Crystalline Solid-State Ion-Selective Electrodes

Solid-state ion-selective electrodes use membranes fashioned from polycrystalline or single-crystal inorganic salts. Polycrystalline ion-selective electrodes are made by forming a thin pellet of Ag_2S, or a mixture of Ag_2S and either a second silver salt or another metal sulfide. The pellet, which is 1–2 mm in thickness, is sealed into the end of a nonconducting plastic cylinder, and an internal solution containing the analyte and a reference electrode are placed in the cylinder. Charge is carried across the membrane by Ag^+ ions.

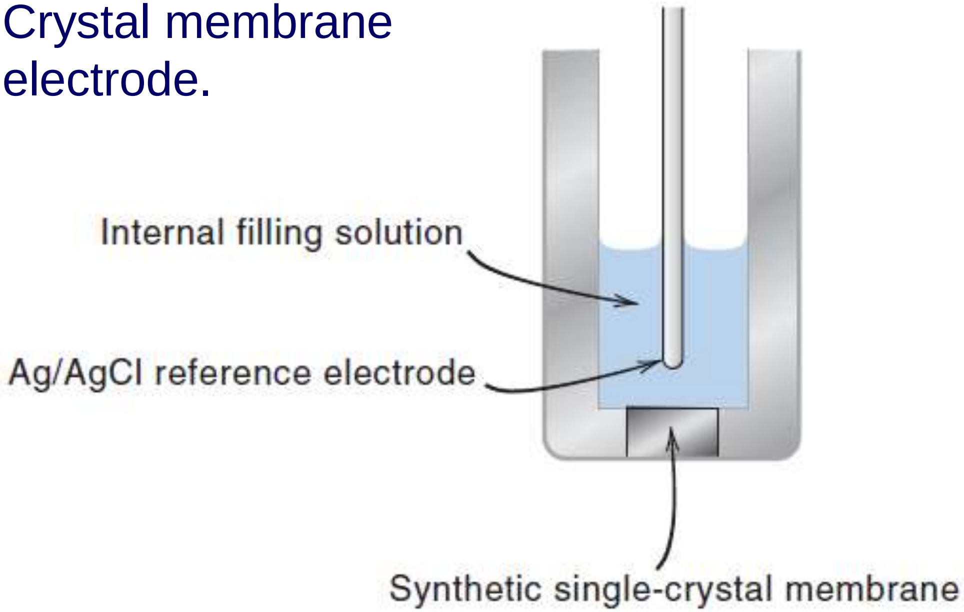
Several examples of polycrystalline, Ag_2S-based ion-selective electrodes are listed. The selectivity of these ion-selective electrodes is determined by solubility. Thus, a Cl^- ion-selective electrode constructed using a Ag_2S/AgCl membrane is more selective for Br^- *and* I^- *since AgBr and* AgI are less soluble than AgCl. If the concentration of Br– is sufficiently high, the AgCl at the membrane–solution interface is replaced by AgBr, and the electrode's response to Cl– decreases substantially. Most of the ion-selective electrodes can be used over an extended range of pH levels. The membrane of a F^- ion-selective electrode is fashioned from a single crystal of LaF_3 that is usually doped with a small amount of EuF_2 to enhance the membrane's conductivity.



The fluoride ion-selective electrode is one of the most successful and useful since the determination of fluoride is rather difficult by most other methods.

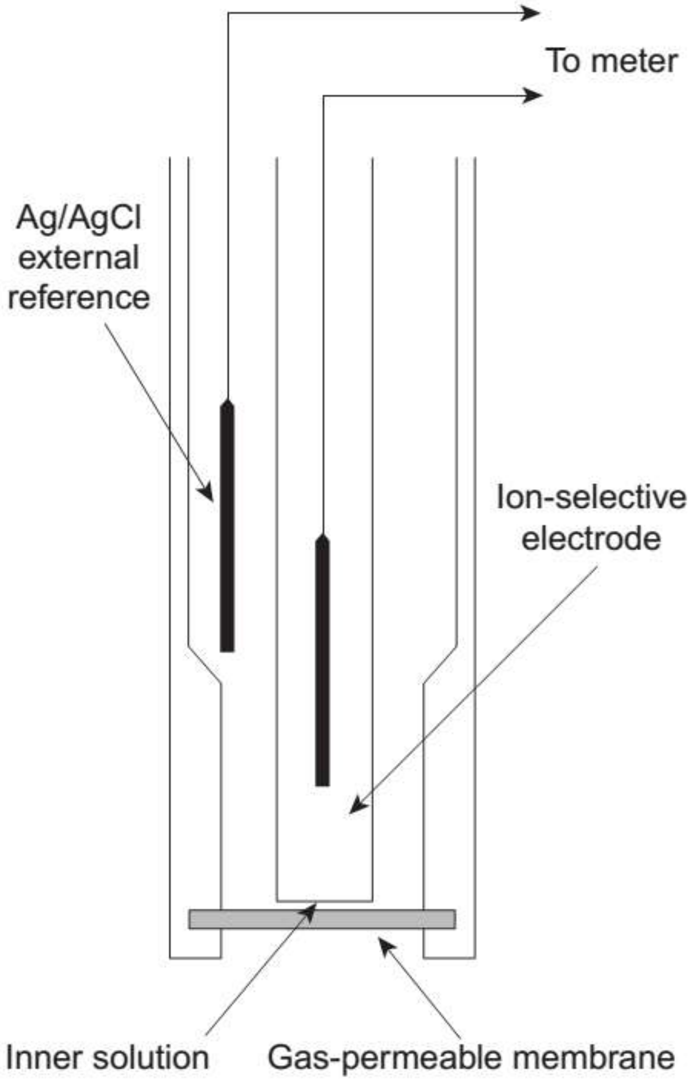
The membrane consists of a single crystal of lanthanum fluoride doped with some europium(II) fluoride to increase the conductivity of the crystal. Lanthanum fluoride is very insoluble, and this electrode exhibits Nerstian response to fluoride down to 10^{-5} *M*. This electrode has at least a 1000-fold selectivity for fluoride ion over chloride, bromide, iodide, nitrate, sulfate, monohydrogen phosphate, and bicarbonate anions and a 10-fold selectivity over hydroxide ion. Hydroxide ion appears to be the only serious interference. The pH range is limited by the formation of hydrofluoric acid at the acid end and by hydroxide ion response at the alkaline end; the useful pH range is 4 to 9.

Crystal membrane electrode.



Gas-Sensing Electrodes

A number of membrane electrodes have been developed that respond to the concentration of dissolved gases.



These electrodes consists of a thin membrane separating the sample from an inner solution containing an ion-selective electrode. The membrane is permeable to the gaseous analyte, but is not permeable to nonvolatile components in the sample matrix. Once the gaseous analyte passes through the membrane, it reacts in the inner solution, producing a species whose concentration can be monitored by an appropriate ion-selective electrode. For example, in the CO_2 electrode, CO_2 reacts in the inner solution to produce H_3O^+.

$$CO_2(aq) + 2H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

The change in the concentration of H_3O^+ is monitored with a pH ion-selective electrode

Evaluation

Scale of Operation

The working range for most ion-selective electrodes is from a maximum concentration of 0.1–1 M to a minimum concentration of 10^{-5} – 10^{-10} M.

Accuracy

The accuracy of a potentiometric analysis is limited by the measurement error for the cell’s potential. Several factors contribute to this measurement error, including the contribution to the potential from interfering ions, the finite current drawn through the cell while measuring the potential, differences in the analyte’s activity coefficient in the sample and standard solutions, and liquid junction potentials. Accuracies of 1–5% for monovalent ions and 2–10% for divalent ions are typical.

Precision

The precision of a potentiometric measurement is limited by variations in temperature and the sensitivity of the potentiometer. Under most conditions, and with simple, general-purpose potentiometers, the potential can be measured with a repeatability of ±0.1 mV. this result corresponds to an uncertainty of ±0.4% for monovalent analytes, and ±0.8% for divalent analytes.

Evaluation

Selectivity

As described earlier, most ion-selective electrodes respond to more than one analyte. For many ion-selective electrodes, however, the selectivity for the analyte is significantly greater than for most interfering ions. Published selectivity coefficients for ion-selective electrodes provide a useful guide in helping the analyst determine whether a potentiometric analysis is feasible for a given sample.

Time, Cost, and Equipment

In comparison with competing methods, potentiometry provides a rapid, relatively low-cost means for analyzing samples. Commercial instruments for measuring pH or potential are available in a variety of price ranges and include portable models for use in the field.