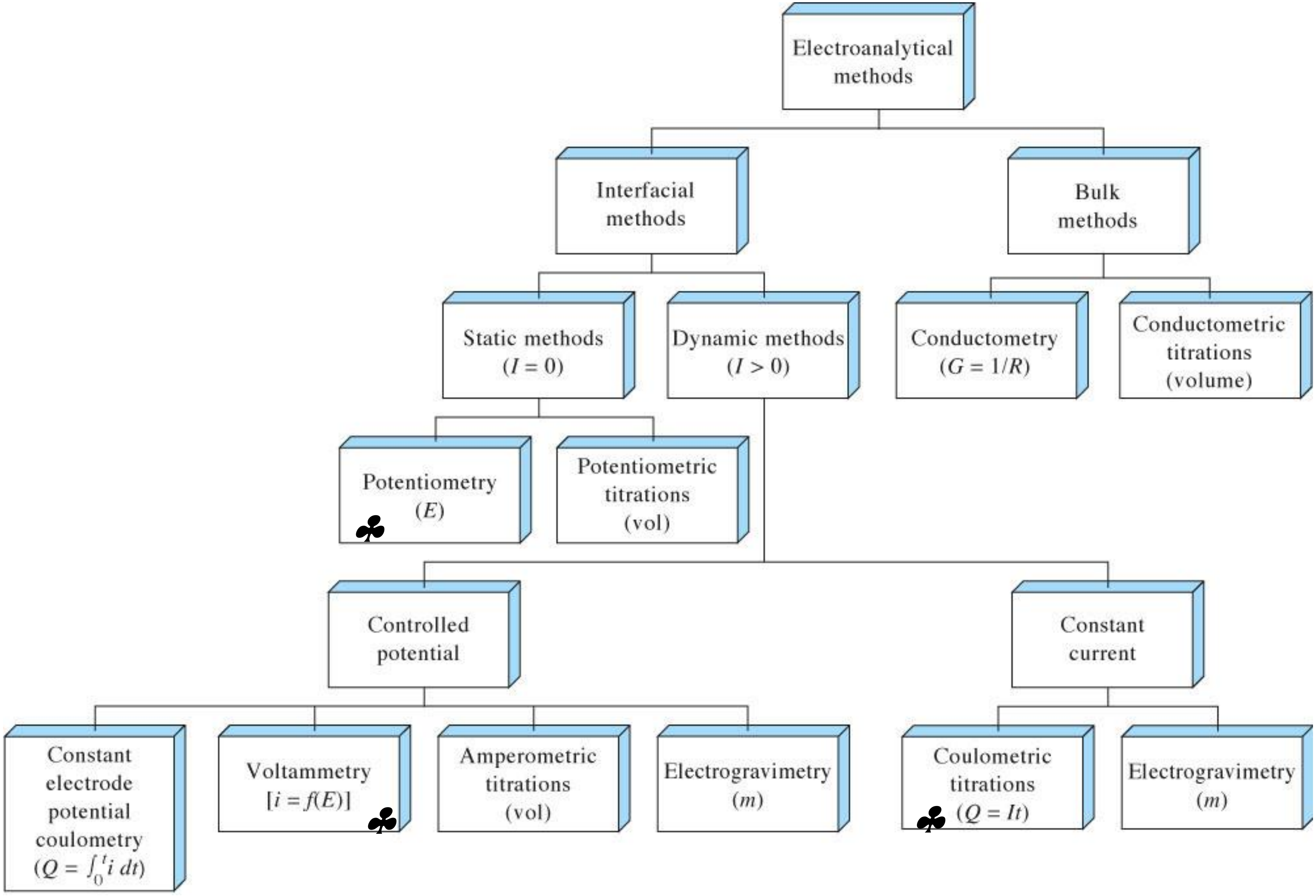
Chapter 22

An Introduction to Electroanalytical Chemistry

- Electroanalytical chemistry encompasses a group of quantitative analytical methods that are based upon the electrical properties of a solution of the analyte when it is made part of an electrochemical cell.
- Electroanalytical methods have certain general advantages over other types of procedures
  - often specific for a particular oxidation state of an element.
  - Instrumentation is relatively inexpensive.
  - Provide information about activities rather than concentrations of chemical species.

B.) Types of Electroanalytical Methods



- Electroanalytical methods
  - Interfacial methods
    - Static methods ($I = 0$)
      - Potentiometry (E) ♣
      - Potentiometric titrations (vol)
    - Dynamic methods ($I > 0$)
      - Controlled potential
        - Constant electrode potential coulometry ($Q = \int_0^t i\,dt$)
        - Voltammetry [$i = f(E)$] ♣
        - Amperometric titrations (vol)
        - Electrogravimetry (m)
      - Constant current
        - Coulometric titrations ($Q = It$) ♣
        - Electrogravimetry (m)
  - Bulk methods
    - Conductometry ($G = 1/R$)
    - Conductometric titrations (volume)

B.) Types of Electroanalytical Methods

Potentiometry:

- measure the potential of electrochemical cells without drawing substantial current

Examples: pH measurements, ion-selective electrodes, titrations

Coulometry:

- measures the electricity required to drive an electrolytic oxid./red. to completion

Examples: titrations, “chloridometers” (AgCl)

Voltammetry:

- measures current as a function of applied potential under conditions that keep a working electrode polarized

- Examples: cyclic voltammetry, many biosensors

ELECTROCHEMICAL CELLS

A dc electrochemical cell consists of two electrical conductors called **electrodes**, each immersed in a suitable electrolyte solution. For a current to develop in a cell, it is necessary

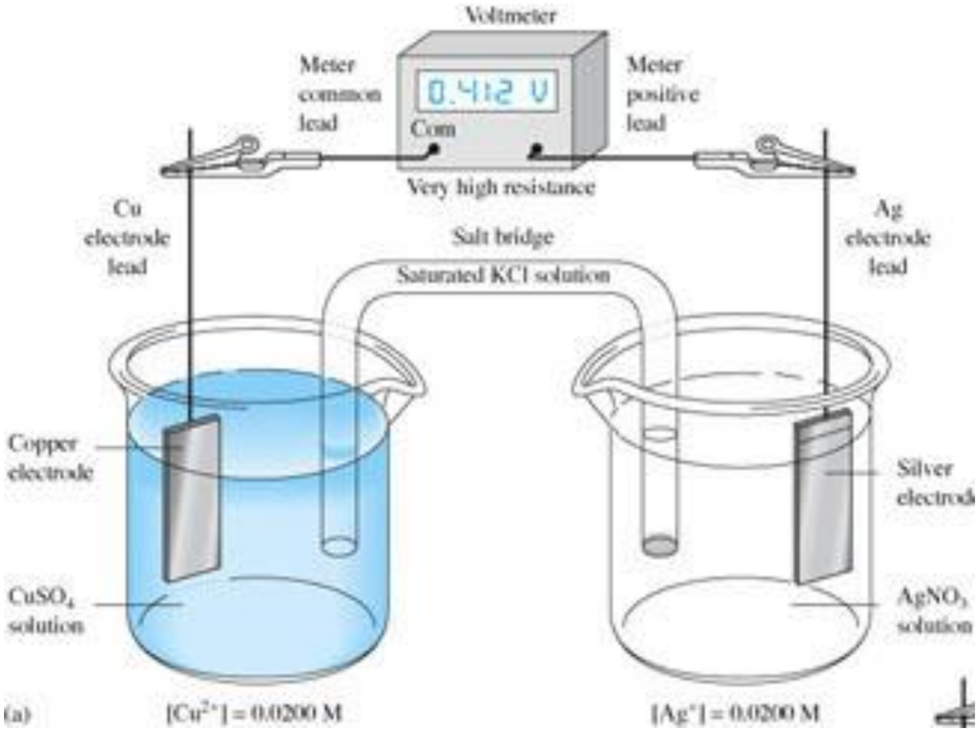
(1) that the electrodes be connected externally by means of a metal conductor,

(2) that the two electrolyte solutions be in contact to permit movement of ions from one to the other, and

(3) that an electron transfer reaction can occur at each of the two electrodes.

salt bridge

- acts to isolate two halves of electrochemical cell while allowing migration of ions and current flow
- usually consists of a tube filled with KCl
- separate species to prevent direct chemical reactions



Conduction in a Cell:

Charge is conducted by three distinct processes in various parts of the cell

1. In the copper and Zinc electrodes, as well as in the external conductor***, electrons serve as carriers***, moving from the zinc through the conductor to the copper.

2. Within the solutions the flow of electricity involves ***migration of both cations and anions***.

In the *half cell on the left*, zinc ions migrate away from the electrode, whereas sulfate and hydrogen sulfate ions move toward it;

In the *half cell on the right*, copper ions move toward the electrode and anions away from it.

Within the *salt bridge*, electricity is carried by migration of potassium ions to the right and chloride ion to the left.

3. A third process occurs at the two electrode surfaces. Here, an oxidation or a reduction reaction provides a mechanism to provide a complete circuit for the flow of charge. The two electrode processes are described by the equations

$$Zn(s) \rightleftarrows Zn^{2+} + 2e^-$$

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

Galvanic and Electrolytic Cells

- The net cell reaction that occurs in the cell shown in Fig. 22-1 is the sum of the two half-cell reactions

$$Zn(s) + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu(s)$$

- Cells, that are operated in a way that produces electrical energy are called galvanic cells.
- Electrolytic cells consume electrical energy, e.g. the cell under discussion could 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.
- If the output of this supply was made somewhat greater than 1.1 V, the two electrode reactions would be reversed and the net cell reaction would become

$$Cu(s) + Zn^{2+} \rightleftharpoons Cu^{2+} + Zn(s)$$

- A cell in which reversing the direction of the current simply reverses the reactions at the two electrodes is termed a **chemically reversible cell**.

Anodes and Cathodes:

- The cathode of an electrochemical cell is the electrode at which reduction occurs, while the anode is the electrode where oxidation takes place.
- The copper electrode is the cathode and the zinc electrode is the anode.

In contrast, where this same cell is operated as an electrolytic cell, the copper electrode would be the anode and the zinc electrode the cathode.

Solution Structure; The Double Layer

- Electrochemical measurements involve heterogeneous systems because an electrode can only donate or accept electrons from a species that is present in a layer of solution that is immediately adjacent to the electrode. Thus, this layer may have composition that differs significantly from that of the bulk of the solution.
- The surface of the metal electrode is shown as having an excess of positive charge as a consequence of an applied positive potential.
- The charged solution layer consists of two parts:
  - (1) a compact inner layer (d_0 to d_1), in which the potential decreases linearly with distance from the electrode surface and

    (2) a diffuse layer (d_1 to d_2), in which the decrease is exponential.

This assemblage of charge at the electrode surface and in the solution adjacent to the surface is termed an **electrical double layer**.

Faradaic and Nonfaradaic Currents

- Two types of processes can conduct currents across an electrode/solution interface.

- One kind involves a direct transfer of electrons via an oxidation reaction at one electrode and a reduction reaction at the other. Processes of this type are called *faradaic* processes because they are governed by Faraday's law, which states that the amount of chemical reaction at an electrode is proportional to the current; the resulting currents are called faradaic currents.

- To understand the basic difference between a faradaic and a nonfaradaic current, imagine an electron traveling down the external circuit to an electrode surface. When the electron reaches the solution interface, it can do one of only two things.
    - It can remain at the electrode surface and increase the charge on the double layer, which constitutes a nonfaradaic current.
    - Alternatively, it can leave the electrode surface and transfer to a species in the solution, thus becoming a part of a faradaic current.

Mass Transfer in Cells with the Passage of Current

A faradaic current requires continuous mass transfer of reactive species from the bulk of the solution to the electrode surface. Three mechanisms bring about this mass transfer:

- **Convection** involves mechanical motion of the solution as a result of stirring or the flow of the solution past the surface of the electrode.
- **Migration** is the movement of ions through the solution brought about by electrostatic attraction between the ions and the charged electrode.
- **Diffusion** is the motion of species brought about by a concentration gradient.

Schematic Representation of Cells

Chemists often employ a shorthand notation, e.g. the cell shown in Fig. 22-1

$$\mathrm{Zn}|\mathrm{ZnSO_4}(a_{\mathrm{Zn\ 2+}} = 0.0100)\ ||\ \mathrm{CuSO_4}(a_{\mathrm{Cu\ 2+}} = 0.0100)|\mathrm{Cu}$$

➢ By convention, the anode and information about the solution with which it is in contact is always listed on the left. Single vertical lines represent phase boundaries across which potential differences may develop.

➢ The cathode is then represented symbolically with another vertical line separating the electrolyte solution from the copper electrode. Because the potential of a cell is dependent upon activities of the cell components, it is common practice to provide activity or concentration data for the cell constituents in parentheses.

The Thermodynamics of Cell Potentials

The potential of an electrochemical cell is related to the activities of the reactants and products of the cell reaction and indirectly to their molar concentrations.

The relationship between the activity of a chemical species and its concentration is given by

$a_X = \gamma_X[X]$ Here, γ_X is the activity coefficient of solute X and the bracketed term is the molar concentration of X.

When the activity coefficient approaches unity, the molar concentration and the activity of a species are identical.

$$2AgCl(s) + H_2(g) \rightleftarrows 2Ag(s) + 2Cl^- + 2H^+$$

The equilibrium constant K for this reaction is given by

$$\boxed{K = \frac{a_{H^+}\, a_{Cl^-}\, a_{Ag}}{p_{H_2}\, a_{AgCl}}}$$

where, a's are the activities of the various species indicated by the subscripts and p_{H2} is the partial pressure of hydrogen in atomospheres.

The activity of a pure solid is unity when it is present in excess (that is, $a_{Ag} = a_{AgCl} = 1.00$)

$$E_{cell} = E_{cell}^0 - RT/nF \ln [(a_{H^+})_i^2 (a_{Cl^-})_i^2]$$ *Nernst equation.*

The standard potential is equal to the cell potential when the reactants and products are at unit activity and pressure.

Liquid Junction Potentials

✓ When two electrolyte solutions of different composition are brought into contact with one another, a potential develops across the interface.

✓ This junction potential arises from an unequal distribution of cations and anions across the boundary due to differences in the rates at which these species diffuse.

Consider the liquid junction in the system

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

✓ Both hydrogen ions and chloride ions tend to diffuse across this boundary from the more concentrated to the more dilute solution, the driving force for this movement being proportional to the concentration difference.

✓ The more dilute side of the boundary becomes positively charged owing to the more rapid diffusion of hydrogen ions; the concentrated side, therefore, acquires a negative charge from the excess of slower-moving chloride ions.

ELECTRODE POTENTIALS

The cell reaction of an electrochemical cell as being made up of two half-cell reactions, each of which has a characteristic electrode potential associated with it. By convention, they are both written as reductions.

$$2AgCl(s) + 2e^- \rightleftarrows 2Ag(s) + 2Cl^-$$

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

To obtain the cell reaction, the second half-reaction is subtracted from the first to give

$$2AgCl(s) + H_2 \rightleftarrows 2Ag(s) + 2H^+ + 2Cl^-$$

That is, $E_{cell} = E_{AgCl} – E_{H+}$ or $E_{cell} = E_{cathode} – E_{anode}$

where, $E_{cathode}$ and E_{anode} are the electrode potentials for the cathodic and anodic half-reactions.

The Standard Hydrogen Electrode (SHE)

- ✓ Hydrogen gas electrodes were widely used not only as reference electrodes but also as indicator electrodes for the determination of pH. The composition of this type of electrode can be represented as

  $$\text{Pt,H}_2(\text{p atm}) \mid \text{H}^+(a_{\text{H+}} = x)$$

- ✓ The potential at the platinum surface depends upon the hydrogen ion activity of the solution and upon the partial pressure of the hydrogen used to saturate the solution.
- ✓ The hydrogen electrode may act as an anode or a cathode, depending upon the half-cell with which it is coupled by means of the salt bridge.
- ✓ Hydrogen is oxidized to hydrogen ions when the electrode is an anode; the reverse reaction takes place as a cathode.
- ✓ For the standard hydrogen electrode call for a hydrogen ion activity of unity and a partial pressure for hydrogen of exactly one atmosphere. By convention, the potential of this electrode is assigned the value of exactly zero volt at all temperatures.

Practical Reference Electrodes

- ✓ The standard hydrogen electrode is of great fundamental importance, the difficulty in preparing the electrode surface and controlling the activities of the reactants make it impractical enough.
- ✓ Reference electrodes that are simple to prepare, more rugged, and easier to use are normally substituted for the hydrogen gas electrode.
- ✓ One of the most common of these is the silver/silver chloride electrode. This electrode can be prepared by applying an oxidizing potential to a silver wire immersed in a dilute solution of hydrochloric acid.
- ✓ The potential of this electrode is about 0.2 V positive with respect to the standard hydrogen electrode. The electrode half-reaction is

$$2AgCl(s) + e^- \rightleftarrows Cl^- + 2Ag(s)$$

- ✓ A second widely used reference electrode is the saturated calomel electrode (SCE), which consists of a pool of mercury in contact with a solution that is saturated with mercury(I) chloride (calomel) as well as potassium chloride. The potential of this reference is about 0.24 V positive. The electrode reaction is

$$Hg_2Cl_2(s) + 2e^- \rightleftarrows 2\,Cl^- + 2Hg(l)$$

Definition of Electrode Potential

Electrode potentials are defined as cell potentials for a cell consisting of the electrode acting as a cathode and the standard hydrogen electrode acting as an anode.

The electrode potential for the half-reaction

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

✓ Here, the half-cell on the right (the cathode) consists of a strip of the metal M in contact with a solution of M^{2+}. The half-cell on the left (the anode) is standard hydrogen electrode. By definition, the potential E observed on the voltage-measuring device is the electrode potential for the M/ M^{2+} couple.

✓ If we assume that the activity of M^{2+} in the solution is exactly 1.00, the potential is called the standard electrode potential for the system and is given the symbol E^0. That is, the standard electrode potential for a half-reaction is the electrode potential when the reactants and products are all at unit activity.

The standard electrode potentials can be arranged in the order

$Cu^{2+} + 2e^{-} \rightleftharpoons Cu(s)$ $E^0 = +0.337$ V

$2H^{+} + 2e^{-} \rightleftharpoons H_2(g)$ $E^0 = 0.000$ V

$Cd^{2+} + 2e^{-} \rightleftharpoons Cd(s)$ $E^0 = -0.403$ V

$Zn^{2+} + 2e^{-} \rightleftharpoons Zn(s)$ $E^0 = -0.763$ V

The magnitudes of these standard electrode potentials show the relative strengths as electron acceptors; $Cu^{2+} > H^{+} > Cd^{2+} > Zn^{2+}$.

Sign Conventions for Electrode Potentials

- According to the IUPAC convention, the term electrode potential is reserved exclusively for half-reaction written as reductions.
- An oxidation potential should never be called an electrode potential.
- The sign of the electrode potential is determined by the actual sign of the electrode of interest when it is coupled with a standard hydrogen electrode in a galvanic cell.
- Thus, a zinc or a cadmium electrode will behave as the anode from which electrons flow through the external circuit to the standard hydrogen electrode.
- These metal electrodes are thus the negative terminal of such galvanic cells, and their electrode potentials are assigned negative values.
- Thus, $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ $E^0 = -0.763\ V$

  $Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$ $E^0 = -0.403\ V$

  The potential for the copper electrode is given a positive sign because the copper behaves as a cathode in a galvanic cell constructed from this electrode and the hydrogen electrode; electrons flow toward the copper electrode through the external circuit. It is thus the positive terminal of the galvanic cell and for copper, we may write

  $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ $E^0 = +0.337\ V$

  The sign of the electrode potential will indicate whether or not the reduction is spontaneous with respect to the standard hydrogen electrode.

Effect of Activity on Electrode Potential

Let us consider the half-reaction

$$pP + qQ + \ldots\ldots + ne^- \rightleftharpoons rR + sS\ldots\ldots$$

where the capital letters represent formulas of reacting species, e- represents the electron, and the lower-case letters indicate the number of moles of each species.

At room temperature (298 K)

$$E = E_0 - \frac{0.0592}{n}\log\frac{(a_R)i^r \ . \ (a_S)i^s \ \ldots\ldots}{(a_P)i^p \ . \ (a_Q)i^q \ \ldots\ldots}$$

Equation is a general statement of the Nernst equation, which can be applied both to half-cell reactions or cell reactions

Substitution of Concentration for Activities:

✓ Molar concentration—rather than activities—of reactive species are generally employed in making computations with the Nernst equation.

✓ The assumption that these two quantities are identical is *valid only in dilute solutions*: with increasing electrolyte concentrations, potentials calculated on the basis of molar concentrations can be expected to depart from those obtained by experiment.

The Standard Electrode Potential, E^0

✓An examination of Nernst equation reveals that the constant E^0 is equal to the half-cell potential when the logarithmic term is zero.

✓This condition occurs whenever the activity quotient is equal to unity, one such instance being when the activities of all reactants and products are unity.

✓Thus, the standard potential is often defined as the electrode potential of a half-cell reaction (vs. SHE) when all reactants and products are present at unit activity.

Effect of Other Equilibria:

The application of standard electrode potentials is further complicated by the occurrence of solvation, dissociation, association, and complex-formation reactions involving the species of interest.

Formal Potentials:

✓ Swift proposed substituting a quantity called the formal potential $E^{0'}$ in place of the standard electrode potential in oxidation/reduction calculations.

✓ In order to compensate partially for activity effects and errors resulting from side reactions.

✓ The formal potential of a system is the potential of the half-cell with respect to the standard hydrogen electrode when the concentrations of reactants and products are 1 M and the concentrations of any other constituents of the solution are carefully specified.

Calculation Of Cell Potentials From Electrode Potentials

✓ An important use of standard electrode potentials is the calculation of the potential obtainable from a galvanic cell or the potential required to operate an electrolytic cell.

✓ The electromotive force of a cell is obtained by combining half-cell potentials as follows: $E_{cell} = E_{cathode} – E_{anode}$

✓Consider a hypothetical cell

$$\boxed{Zn|ZnSO_4(a_{Zn2+} = 1.00)||CuSO_4\ (a_{Cu2+} = 1.00)|Cu}$$

using E^0 data from Table 22-1, $E_{cell} = +0.337 –(-0.763) = +1.100$ V

The positive sign for the cell potential indicates that the reaction

$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$ occurs *spontaneously and this is a galvanic cell*.

✓ The foregoing cell, diagrammed as $\boxed{Cu|Cu^{2+}(a_{Cu2+} = 1.00)||\ Zn^{2+}(a_{Zn2+} = 1.00)|Zn}$

implies that the copper electrode is now the anode. Thus,

$$E_{cell} = -0.763 –(+0.337) = -1.100 \text{ V}$$

The negative sign indicates the nonspontaneity of the reaction

$Cu(s) + Zn^{2+} \rightarrow Cu^{2+} + Zn(s)$ The application of an external potential greater than 1.100 V is required to cause this reaction to occur.

22E Currents In Electrochemical Cells

✓ Except potentiometric methods all electroanalytical methods involve electrical currents and current measurements. We need to consider the behavior of cells when significant currents are present.

✓ Electricity is carried within a cell by the movement of ions. With small currents, Ohm's law is usually obeyed, and we may write E = IR where E is the potential difference in volts responsible for movement of the ions, I is the current in amperes, and R is the resistance in ohms of the electrolyte to the current.

✓The measured cell potential normally departs from that derived from theoretical thermodynamic calculation. This departure can be traced to a number of phenomena, including:

- ✓ ohmic potential and
- ✓ several polarization effects, such as :
  - ✓charge-transfer polarization,
  - ✓concentration polarization,
  - ✓diffusion overvoltage, and
  - ✓crystallization overvoltage.
- ✓Generally, these phenomena have the effect of reducing the potential of a galvanic cell or increasing the potential needed to develop a current in an electrolytic cell.

22E-1 Ohmic Potential; IR Drop

- To develop a current in either a galvanic or an electrolytic cell, a driving force in the form of a *potential is required to overcome the resistance of the ions to movement toward the anode and the cathode.*

- This force follows Ohm’s law and is equal to the product of the current in amperes and the resistance of the cell in ohms. The force is generally referred to as the ohmic potential, or the IR drop.

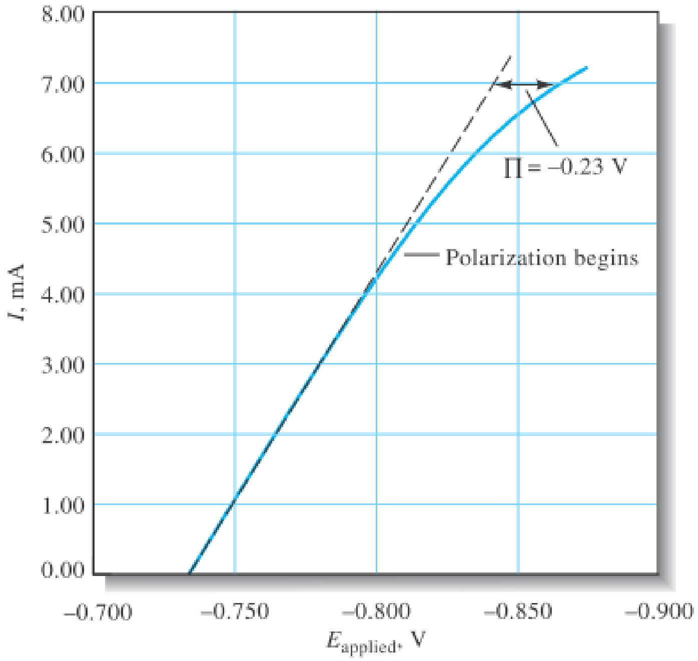
- The net effect of IR drop is to increase the potential required to operate an electrolytic cell and to decrease the measured potential of a galvanic cell. Therefore, the IR drop is always subtracted from the *theoretical cell potential*.

$$E_{applied} = E_{cathode} – E_{anode} - IR$$

22E-2 Polarization

✓ In several important electroanalytical methods we measure the current in a cell as a function of potential and construct current versus voltage curves from the data. Equation 22-16 $E_{applied} = E_{cathode} – E_{anode} - IR$ predicts a linear relationship between the cell voltage and the current at constant electrode potentials.

✓ In fact, current-voltage curves are frequently nonlinear at the extremes; under these circumstances, the cell is polarized. Polarization may occur at one or both electrodes.



Experimental current/voltage curve for operation of the cell.

- The term polarization refers to the deviation of the electrode potential from the value predicted by the Nernst equation on the passage of current.
- Cells that exhibit nonlinear behavior at higher currents exhibit polarization, and the degree of polarization is given by an overvoltage, or overpotential, which is symbolized by Π.

$$E_{applied} = E_{cell} – IR – \Pi$$

Factors that influence polarization are
(1) electrode size, shape, and composition;
(2) composition of the electrolyte solution;
(3) temperature and stirring rate;
(4) current level; and
(5) physical state of the species participating in the cell reaction.

Polarization phenomena can be divided into two categories:

a) concentration polarization and
b) kinetic polarization.

Concentration polarization occurs because of the finite rate of mass transfer from the solution to the electrode surface.

It occurs when reactant species do not arrive at the surface of the electrode or product species do not leave the surface of the electrode fast enough to maintain the desired current.

Reactants are transported to the surface of an electrode by three mechanisms: *diffusion, migration, and convection.*

Products are removed from electrode surfaces in the same ways.

Diffusion

Whenever there is a concentration difference between two regions of a solution, as happens when a species is reduced at a cathode surface (or oxidized at an anode surface), diffusion causes ions or molecules to move from the more concentrated region to the more dilute. The rate of diffusion *is given by*

$$dc / dt = k(c-c_0)$$

c is the reactant concentration in the bulk of the solution,
C_o is its equilibrium concentration at the electrode surface, and
k is a proportionality constant.

As shown earlier, *the value of* C_0 *is fixed by the potential of the electrode and can be calculated from the Nernst equation.* As increasingly higher potentials are applied to the electrode, C_0 becomes smaller and smaller, and the diffusion rate becomes greater and greater.

Ultimately, however, C_0 becomes negligible with respect to c, and the rate then becomes constant. That is, when $C_0 \rightarrow 0$, $dc / dt = k c$

Under this condition, concentration polarization is said to be complete, and the electrode operates as an ideal polarized electrode

Convection is the transport of ions or molecules through a solution as a result of stirring, vibration, or temperature gradients. Thus, forced convection, such as stirring or agitation, tends to decrease concentration polarization.

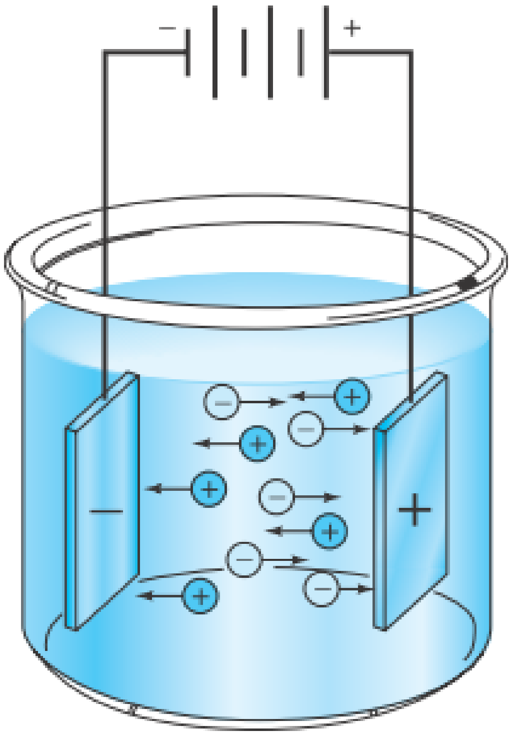


Figure 22-5 The motion of ions through a solution because of the electrostatic attraction between the ions and the electrodes is called migration.

Migration is the process by which ions move under the influence of an electrostatic field. It is often the primary mass-transfer process in the bulk of the solution in a cell. The electrostatic attraction (or repulsion) between a particular ionic species and the electrode becomes smaller as the total electrolyte concentration of the solution becomes greater. It may approach zero when the reactive species is only a small fraction, say 1/100,of the total concentration of ions with a given charge.

To summarize, concentration polarization is observed when diffusion, migration, and convection are insufficient to transport the reactant to or from an electrode surface at a rate demanded by the theoretical current.
Because of concentration polarization, a larger potential must he applied to an electrolytic cell than the value predicted from the thermodynamic potential and the *IR drop.*

Charge-Transfer Polarization

✓ Charge-transfer polarization arises when the rate of the oxidation or reduction reaction at one or both electrodes is not sufficiently rapid to yield currents of the size demanded. The overvoltage arising from charge-transfer polarization has the following characteristics:

1. Overvoltages increase with current density (current density is defined as the amperes per square centimeter of electrode surface)
2. Overvoltages usually decrease with increases in temperature.
3. Overvoltages vary with the chemical composition of the electrode.
4. Overvoltages are most marked for electrode processes that yield gaseous products such as hydrogen or oxygen; they are frequently negligible where a metal is being deposited or where an ion is under going a change of oxidation state.
5. The magnitude of overvoltage in any given situation cannot be predicted exactly because it is determined by a number of uncontrollable variables.

- ✓ To begin our discussion, it is useful to consider current-voltage curves for an *ideal polarized and an ideal nonpolarized electrode.* Polarization at a single electrode can be studied by coupling it with an electrode that is not easily polarized.
- Such electrodes have large surface areas and have half-cell reactions that are rapid and reversible. Design details of nonpolarized electrodes are described in subsequent chapters.