



Chem 306 Instrumental Analysis II

Prof. Dr. Şerife H. Yalçın

İzmir Institute of Technology, Chemistry Dept. 35430 İZMİR/TURKEY

Informations given in these slides are, either in part or all, recollection from the following sources, solely for education purposes.

Principles of Instrumental Analysis, 6e/7e by Holler, Skoog & Crouch, 2007

Fundamentals of Analytical Chemistry 9e by Douglas A. Skoog, 2013.

Chapter 22

An Introduction to Electroanalytical Chemistry

Introduction

- 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 techniques are capable of producing low detection limits and a wealth of characterization information describing electrochemically accessible systems. such information includes:
 - the stoichiometry and rate of interfacial charge transfer,
 - the rate of mass transfer,
 - the extent of adsorption or chemisorption, and
 - the rates and equilibrium constants for chemical reactions.

General Advantages of Electrochemistry

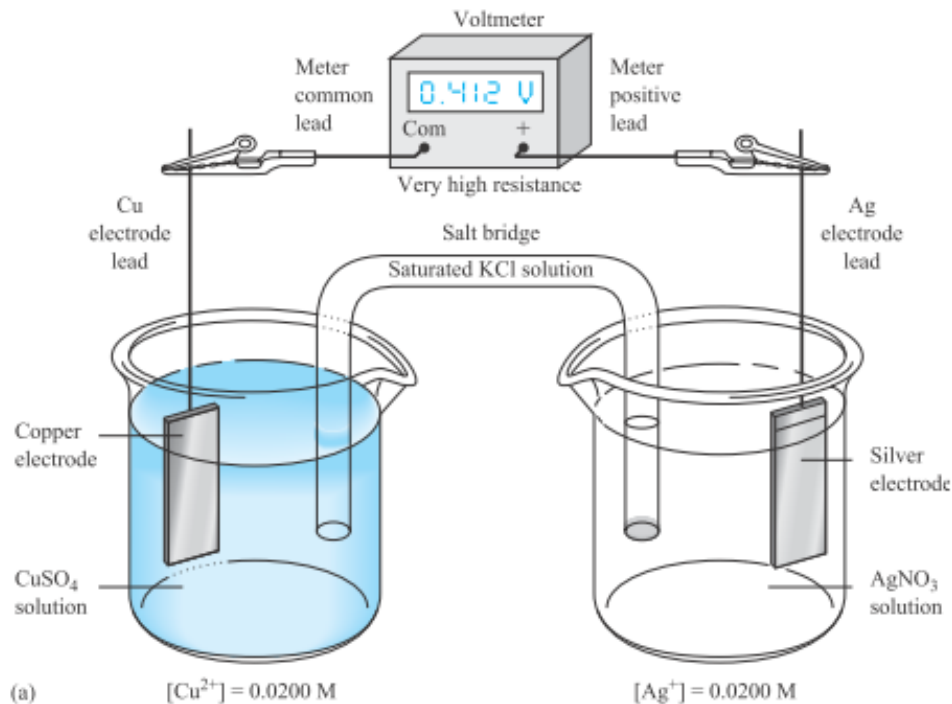
- Electroanalytical methods have certain general advantages over other types of procedures
 - often selective for a particular oxidation state of an element.
 - » e.g. a mixture of cerium(III) and cerium(IV)
 - Instrumentation is relatively inexpensive.
 - » cost - \$ 8,000 - \$25,000 for a good instrument compared to \$ 50,000 - \$250,000 for a good spectrophotometer
 - Provide information about activities rather than concentrations of chemical species.
 - » activity usually of more physiological importance
 - Fast, in-situ

22A ELECTROCHEMICAL CELLS

A dc electrochemical cell consists of two electrical conductors called **electrodes**, each immersed in a suitable **electrolyte** solution.

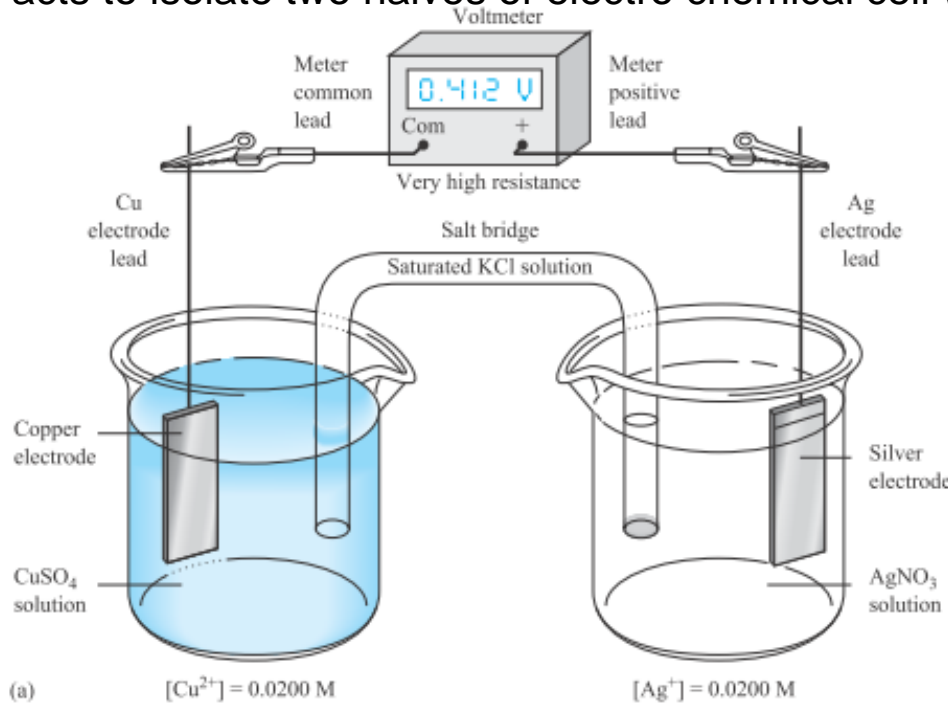
For a current to develop in a cell, it is necessary

- 1) external connection between electrodes, by means of a metal conductor (wire),
- 2) internal connection via contact with a common solution or by different solutions connected by a salt bridge.
- 3) that an electron-transfer reaction can occur at each of the two electrodes.



Salt bridge

- acts to isolate two halves of electro chemical cell while allowing migration of ions and current



- usually consists of a tube filled with a solution sat'd with KCl
- The two ends of the tube are fitted with porous plugs or disks that permit the movement of ions across them but prevent siphoning of liquid from one electrolyte solution to the other.

The cells in Figure 22-1 contain two so-called liquid junctions,

- one being the interface between the silver nitrate solution and the salt bridge;
- the second is at the other end of the salt bridge where the electrolyte solution of the bridge contacts the copper sulfate solution.

A small junction potential at each of these interfaces may influence significantly the accuracy of the analysis.

22A-1 Conduction in a Cell:

- When a voltmeter of high internal resistance is connected, the cell is said to be at open circuit and delivers the full cell potential.
- The voltage developed in the cell is measured without drawing significant current from the cell.

- If we replace the high-impedance meter in Figure 22-1a with a low-resistance wire or load as shown in Figure 22-1b, the circuit is completed, and charge flows.
- Charge conduction results from three distinct processes in various parts of the cell shown in Figure 22-1b:

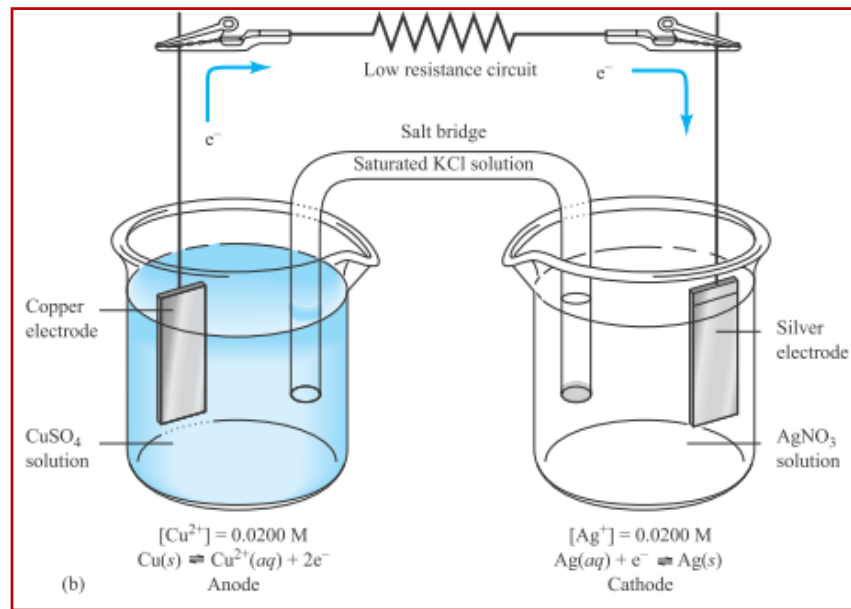
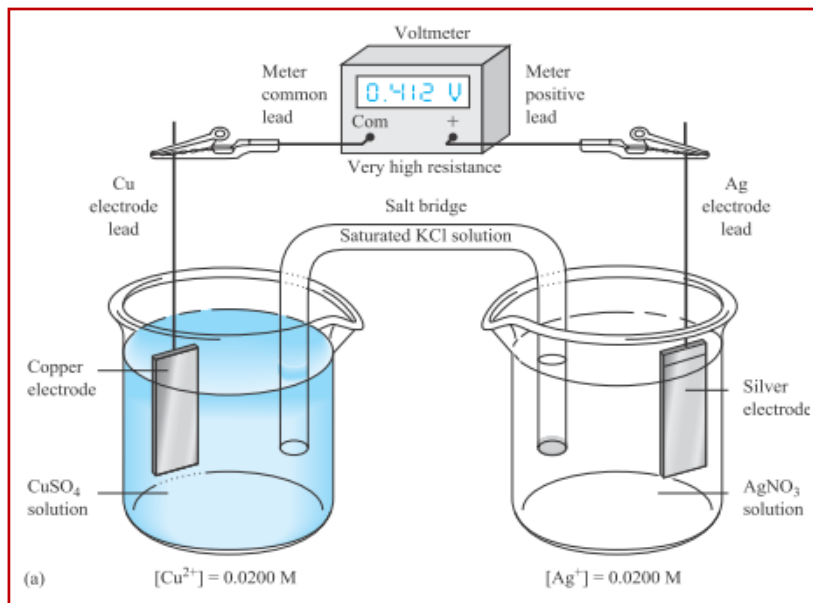


FIGURE 22-1 (a) A galvanic electrochemical cell at open circuit; (b) a galvanic cell doing work;

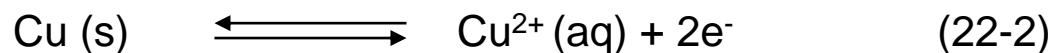
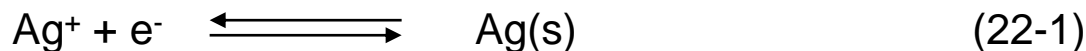
22A-1 Conduction in a Cell:

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

1. In the copper and silver electrodes, as well as in the external conductor, **electrons are the charge carriers**, moving from the copper electrode through the external conductor to the silver electrode.
2. Within the solutions of each half cell, the flow of electricity involves **migration of both cations and anions**.
 - * In the **half cell on the left**, copper ions migrate away from the electrode, whereas sulfate and hydrogen sulfate ions move toward it;
 - * In the **half cell on the right**, silver ions move toward the electrode and anions away from it.
 - * Within the **salt bridge**, charge is carried by migration of potassium ions to the right and chloride ion to the left.

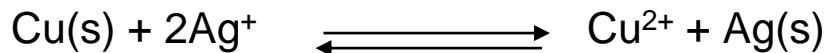
Thus, all of the ions in the three solutions participate in the flow of charge.

3. A third process occurs at the two electrode surfaces. Here, an oxidation or a reduction rxn couples the ionic conduction of the solution with the electron conduction of the electrode to provide a complete circuit for the flow of charge. The two electrode processes are described by



22A-2 Galvanic and Electrolytic Cells

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



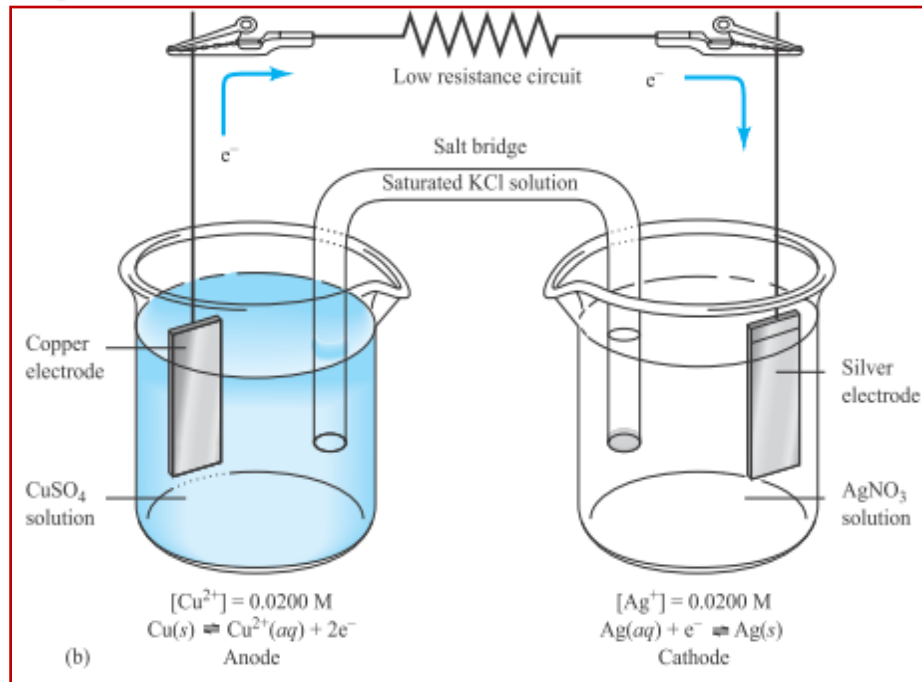
- The voltage of this cell is a measure of the tendency for this reaction to proceed toward equilibrium. Thus, when the copper and silver ion concentrations (actually, activities) are 0.0200 M, the cell voltage is 0.412 V.

- This shows that the reaction is far from equilibrium.

- If we connect a resistor or other load in the external circuit as shown in Figure 22-1b, a measurable current in the circuit results and the cell reaction occurs.

- As the reaction proceeds, the voltage becomes smaller and smaller, and it ultimately reaches 0.000 V when the system achieves equilibrium.

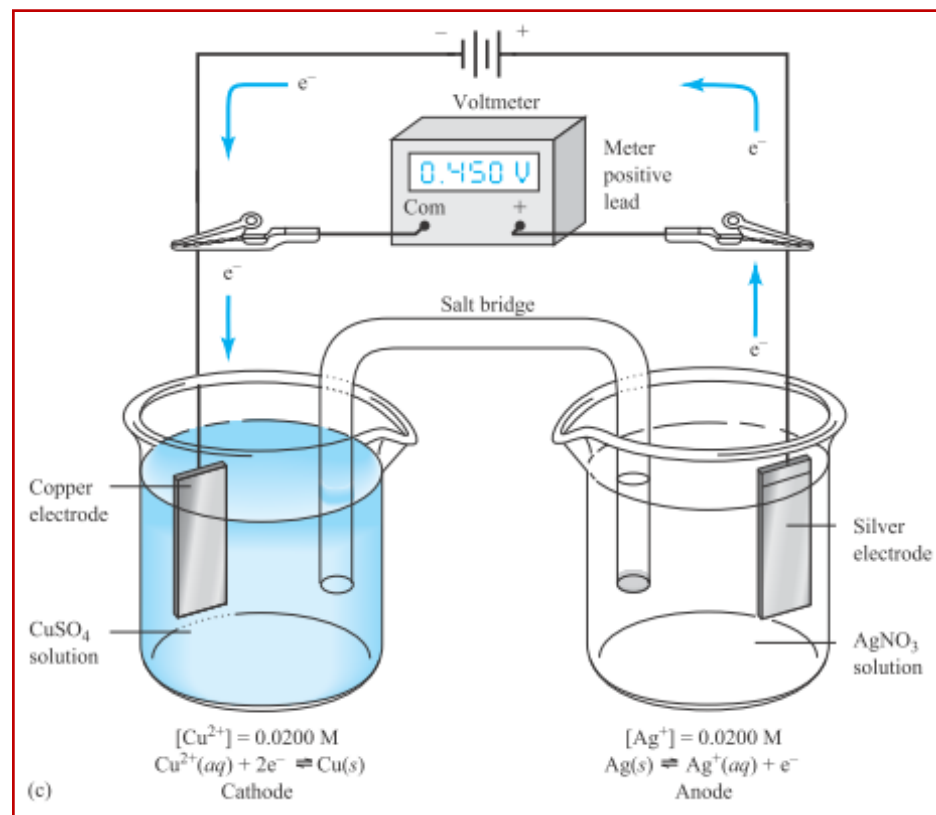
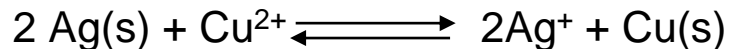
- Cells, that are operated in a way that produces electrical energy are called **galvanic cells**.



Galvanic Cells;

- reaction occurs naturally
- positive potential ($E_{\text{cell}} = +$)
- exothermic
- produces energy

- **Electrolytic cells**, in contrast 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 copper electrode and the positive terminal to the silver electrode.
- If the output of this supply was made somewhat greater than 0.412 V, the two electrode reactions would be reversed and the net cell reaction would be

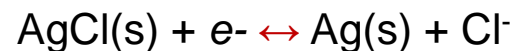
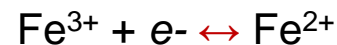
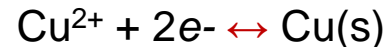


➤ A cell in which reversing the direction of the current simply reverses the reactions at the two electrodes is termed a **chemically reversible cell**.

22A-3 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.
- These definitions apply to both galvanic cells under discharge and to electrolytic cells
- For the galvanic cell shown in Fig. 22-1b The silver electrode is the cathode and the copper electrode is the anode.
- In contrast, where this same cell is operated as an electrolytic cell, the silver electrode would be the anode and the copper electrode the cathode.

Examples of cathode ½ reactions:

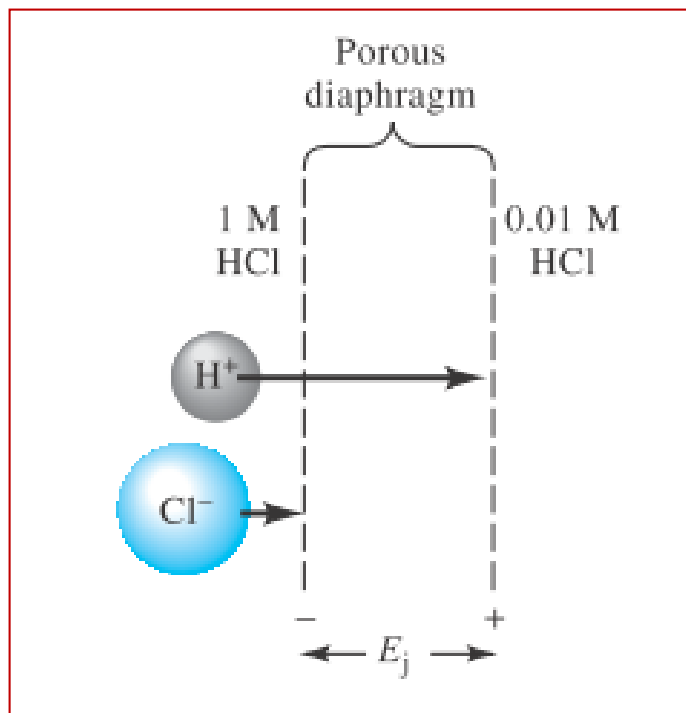


Examples of anode ½ reactions:



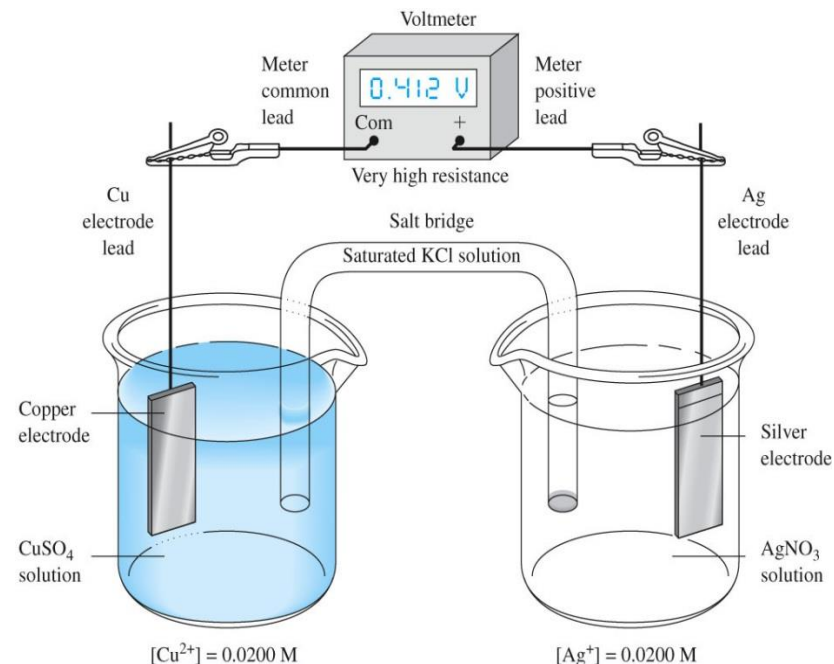
Liquid Junction Potentials:

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



The liquid junction may be represented as:
 $HCl(1\ M) \mid HCl(0.01\ M)$.

The lengths of the arrows correspond to the relative mobilities of the ions



The cell shown in Figure 22-1 has two liquid junctions,

- one between the silver nitrate solution and one end of the salt bridge,
- the other between the copper sulfate solution and the salt bridge.

Small junction potentials may develop at junctions that affect overall cell potential

22A-4 Cells without Liquid Junctions:

➤ To eliminate the effect of junction potentials, sometimes it is possible and advantageous to prepare cells in which the electrodes share a common electrolyte. **Cells without Liquid Junctions**

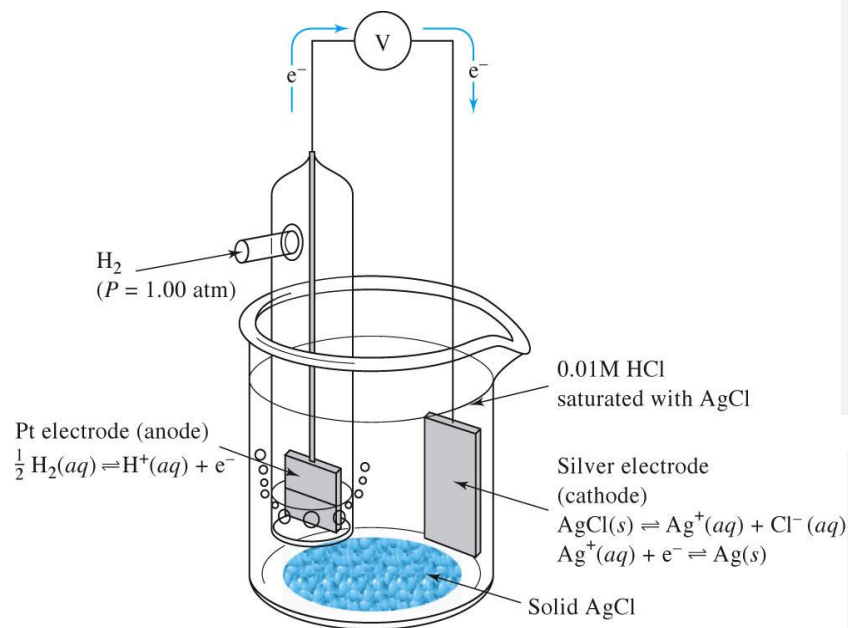


Figure 22-2 a galvanic cell without a liq. junction

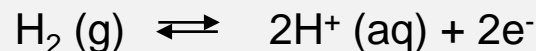
➤ Hydrogen gas is bubbled across the surface of a Pt electrode so that the conc. of the gas at the surface is const. at const. temp. and const. partial pressure of H_2

➤ In this case the inert Pt electrode plays no direct role in the rxn but serves only as a surface where electron transfer can occur.

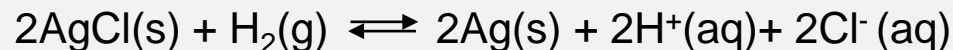
➤ If the voltmeter were removed and replaced by a wire, silver would behave as the **cathode**. The rxn:



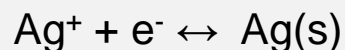
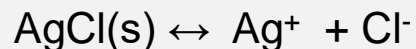
➤ Under discharge, hydrogen is consumed at the platinum **anode**:



➤ Overall:

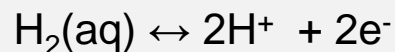
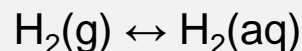


- The cathode reaction in this cell is interesting because it can be considered the result of a two-step process described by the equations



- The slightly soluble silver chloride dissolves in the first step to provide an essentially constant concentration of silver ions that are then reduced in the second step.

- The anodic reaction in this cell is also a two-step process that can be formulated as



- The cell in Figure 22-2 is a galvanic cell with a potential of about 0.46 V. This cell is also chemically reversible and can be operated as an electrolytic cell by applying an external potential of somewhat greater than 0.46 V. Note that you cannot tell whether a given electrode will be a cathode or an anode unless you know whether the cell is galvanic under discharge or electrolytic.

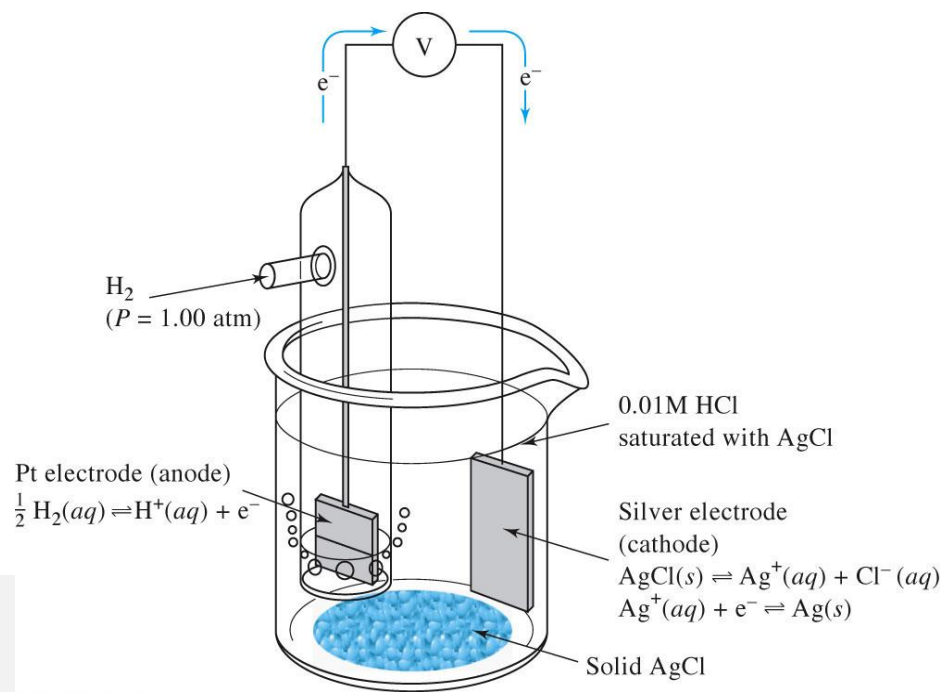
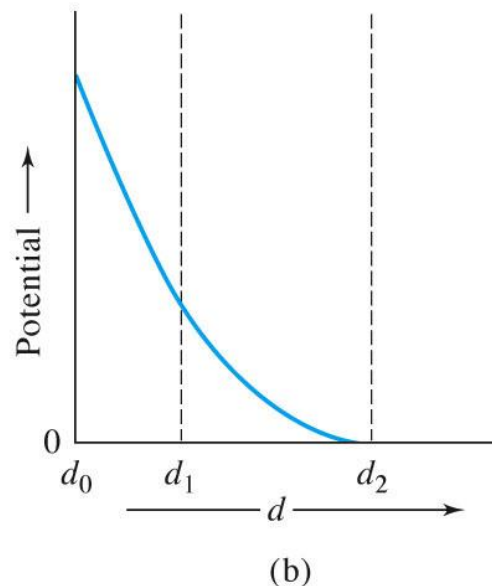
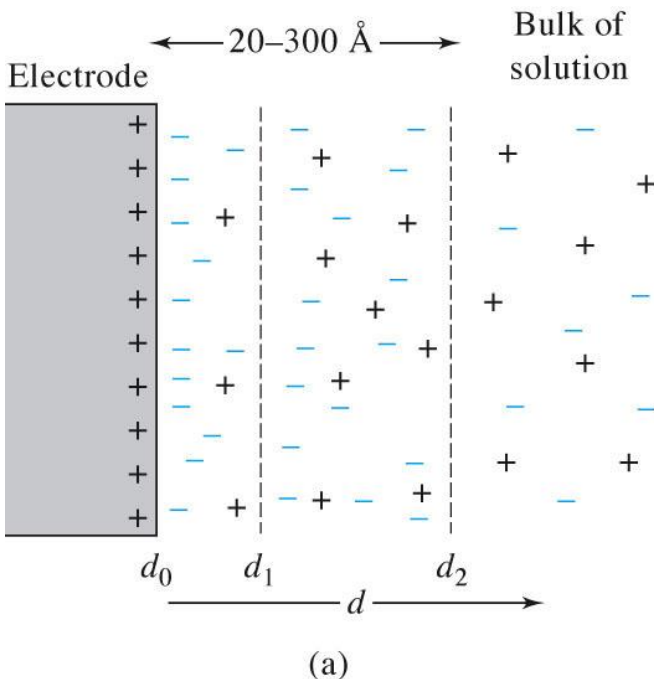


Figure 22-2 Galvanic cell without a liq. junction.

22A-5 Solution Structure: The Electrical Double Layer

- Electrochemical measurements are made on heterogeneous systems.
- 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, *usually within a few angstroms*.
- Thus, as a result of the chemical and physical changes that occur at the electrode-solution interface, 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) Tightly bound inner layer (d_0 to d_1), potential decreases linearly with distance from the electrode surface
 - (2) Loosely bound diffuse layer (d_1 to d_2), in which the potential decrease is exponential wrt distance.



This assemblage of charged species and oriented dipoles (such as water molecules) at the electrode-solution interface is called the **electrical double layer**.

22A-6 Faradaic and Nonfaradaic Currents

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

1. Faradaic processes;

- direct transfer of e^- s via an oxidation rxn at one electrode and a reduction rxn at the other.
- governed by Faraday's law, which states that the amount of chemical rxn at an electrode is proportional to the current; called faradaic currents.

2. Non-Faradaic Processes

- due to processes other than redox reactions at electrodes

example – **charging current**: when first apply potential to the electrode, get redistribution of ions near its surface to counter charge on electrode

- *movement of ions = current*

- as system approaches equilibrium → get decrease in ion movement and current

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.

22A-7 Mass Transfer in Cells with the Passage of Current

- An electrode can probe only a very thin layer of solution at the electrode surface (d_0 to d_1 in Figure 22-3a, ca. 1-100 Å), therefore, 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.

22A-8 Schematic Representation of Cells

Chemists often employ a shorthand notation to simplify the description of cells

e.g. the cell shown in Fig. 22-1



- 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 double vertical line represents two phase boundaries, one at each end of the salt bridge
- There is a liquid-junction potential across each of these interfaces.
- The cathode is then represented symbolically with another vertical line separating the electrolyte solution from the silver electrode.
- Because the potential of a cell is depends on the activities of the cell components, it is common practice to provide activity or concentration data for the cell constituents in parentheses.

22B POTENTIALS IN ELECTROANALYTICAL CELLS

- In most electroanalytical methods, we measure either
 - (1) the current in an electrochemical cell at a fixed potential or
 - (2) the potential of a cell while the current is fixed at some constant level or is zero.

22B-1 The Thermodynamics of Cell Potentials

- The potential of an electrochemical cell is related to the activities of the reactants and products of the cell rxn and indirectly to their molar concentrations
- Although we often make the approximation that these activities are equal to molar concentrations, always remember that this assumption may produce errors in calculated potentials.
- The relationship between the activity of a chemical species and its concentration is given by

$$a_X = \gamma_X [X] \quad \text{Here, } \gamma_X \text{ is the activity coefficient of solute X and}$$

$[X]$ is the molar concentration of X.

When activity coeff. approaches unity, the molar conc. and the activity of a species are identical.

How do the activities of reactants and products affect the potential of a cell?

Consider the cell $2\text{AgCl}(s) + \text{H}_2(g) \rightleftharpoons 2\text{Ag}(s) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq)$

The thermodynamic equilibrium constant K for this rxn is

Where:

a 's are the activities of the various species and p_{H_2} is the partial pressure of H_2 in atmospheres.

$$K = \frac{a_{\text{H}^+}^2 \cdot a_{\text{Cl}^-}^2 \cdot a_{\text{Ag}}^2}{p_{\text{H}_2} \cdot a_{\text{AgCl}}^2} \quad (22-4)$$

- we previously show that the activity of a pure solid is unity when it is present in excess (that is, $a_{\text{Ag}} = a_{\text{AgCl}} = 1.00$). Therefore, Equation 22-4 simplifies to

$$K = \frac{a_{\text{H}^+}^2 \cdot a_{\text{Cl}^-}^2}{p_{\text{H}_2}} \quad (22-5)$$

- It is convenient to define the activity quotient Q such that

$$(22-6) \quad Q = \frac{(a_{\text{H}^+})_i^2 (a_{\text{Cl}^-})_i^2}{(p_{\text{H}_2})_i}$$

The subscript i indicates that the terms in the parentheses are instantaneous activities and not equilibrium activities. The quantity Q , therefore, is not a constant but changes continuously until equilibrium is reached; at that point, Q becomes equal to K , and the i subscripts are deleted.

The change in free energy ΔG for a cell rxn (that is, the maximum work obtainable at constant temperature and pressure) is given by

$$\Delta G = RT \ln Q - RT \ln K = RT \ln \frac{Q}{K}$$

(22-7)

The cell potential E_{cell} is related to the free energy of the reaction by the relationship

$$\Delta G = -nFE_{\text{cell}} \quad (22-8)$$

F : faraday const. (96,485 coulombs/ mole e^- s)
 n : number of moles of e^- s associated with the oxidation-reduction process (in this ex. $n = 2$).

When Equations 22-6 and 22-8 are substituted into 22-7 and the resulting equation is rearranged

$$E_{\text{cell}} = -\frac{RT}{nF} \ln Q + \frac{RT}{nF} \ln K = -\frac{RT}{nF} \ln \frac{(a_{\text{H}^+})_i^2 (a_{\text{Cl}^-})_i^2}{(p_{\text{H}_2})_i} + \frac{RT}{nF} \ln K \quad (22-9)$$

The last term in this equation is a constant, which is called the standard potential for the cell, E_{cell}^0

$$E_{\text{cell}}^0 = \frac{RT}{nF} \ln K$$

(22-10)

Substitution of
Equation 22-10 into
Equation 22-9 yields

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{(a_{\text{H}^+})_i^2 (a_{\text{Cl}^-})_i^2}{(p_{\text{H}_2})_i}$$

(22-11)

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

Equation 22-11 is a form of the Nernst equation, named in honor of Walther Nernst (1864–1941), German physical chemist and winner of the 1920 Nobel Prize in Chemistry. This equation is used throughout electroanalytical chemistry and forms the basis for many applications.

22B-2 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



✓ 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.

✓ 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.

✓ The junction potential difference resulting from this charge separation may amount to 30 mV or more.

✓ The magnitude of the junction potential can be greatly reduced by a salt bridge between the two solutions.

✓ As the concentration of the salt increases, effectiveness of a salt bridge improves also as the difference between the mobilities of the positive and negative ions of the salt approaches zero. Sat'd KCL solution is very effective from both standpoints.

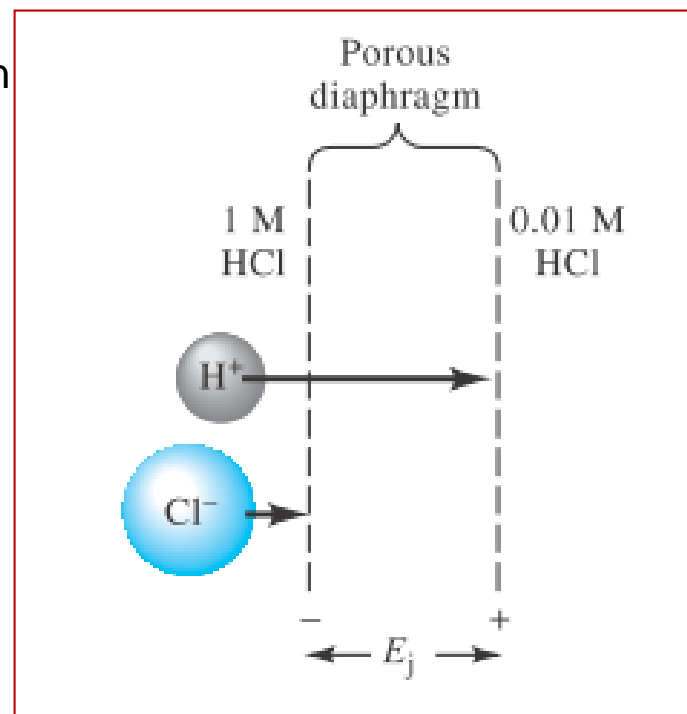


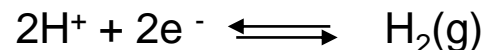
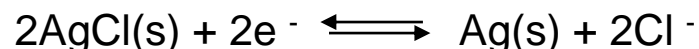
FIGURE 22-4 schematic representation of a liquid junction showing the source of the junction potential E_j . The length of the arrows corresponds to the relative mobility of the two ions.

22C 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.



For the cell, $\text{Pt, H}_2(1 \text{ atm}) | \text{H}^+(0.01 \text{ M}), \text{Cl}^-(0.01 \text{ M}), \text{AgCl}(\text{sat'd}) | \text{Ag}$



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



That is, $E_{\text{cell}} = E_{\text{AgCl}} - E_{\text{H}^{+}}$ or $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$

where, E_{right} and E_{left} are the electrode potentials for the cathodic and anodic half-reactions.

22C-1 Nature of Electrode Potentials

- $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$ This potential is a measure of an electrode's electron energy.
- no method can determine the absolute value of the *potential of a single electrode*, because all voltage measuring devices determine only differences in potential.
- Our inability to measure absolute potentials for half-cell processes is not a serious problem because relative half-cell potentials, measured *versus a common reference electrode*, are just as useful.
- These relative potentials can be combined to give real cell potentials. In addition, they can be used to calculate equilibrium constants of oxidation-reduction processes.
- If E° is "+", it indicates that the reaction is favored or spontaneous. If E° is "-", it indicates that the reaction is not favored or spontaneous and requires energy to proceed
- To develop a useful list of relative half-cell or electrode potentials, we must have a carefully defined reference electrode that is adopted by the entire chemical community.
- The SHE or the normal hydrogen electrode are usually chosen.

22C-2 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 $\text{Pt}, \text{H}_2(p \text{ atm}) \mid \text{H}^+(a_{\text{H}^+} = x)$

✓ The metal conductor Pt has been coated, or **platinized**, with finely divided Pt powder (Pt- black) to increase its specific surface area.

✓ This Pt electrode is immersed in an aqueous acid solution of known, constant hydrogen ion activity. The solution is kept saturated with stream of hydrogen by bubbling the gas at constant pressure over the surface of the electrode.

✓ The platinum does not take part in the electrochemical reaction and serves only as the site where electrons are transferred. Platinum black has a very large surface area to ensure that the reaction is rapid at the electrode surface.

✓ For the SHE for $a_{\text{H}^+} = 1$ and $p_{\text{H}_2} = 1 \text{ atm.}$, by convention, the potential of this is assigned the value of exactly zero volt at all temperatures. $E_{\text{SHE}} = 0\text{V}$

✓ The hydrogen electrode may act as positive /negative electrode. Generally, potentials of other electrodes are compared to SHE using electrode in question as cathode and SHE as anode.

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

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{SHE}}$$

$$E_{\text{cell}} = E_{\text{cathode}} - 0$$

$$E_{\text{cell}} = E_{\text{cathode}}$$

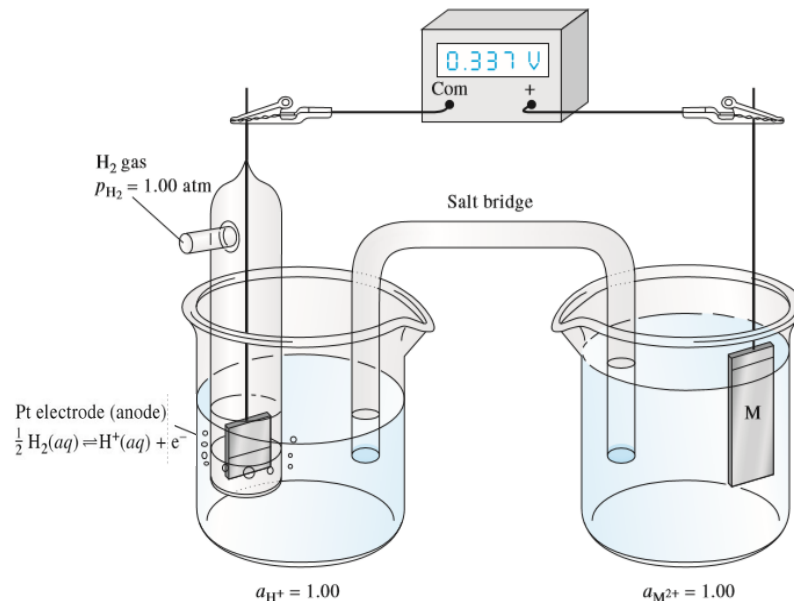
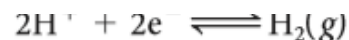


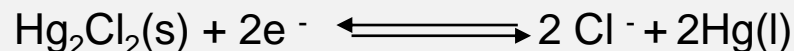
FIGURE 22-5 Measurement of the electrode potential for an M electrode. If the M^{2+} ion activity in the right-hand compartment is 1.00, the cell potential is the standard electrode potential of the half-reaction $\text{M}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{M}(\text{s})$.



22C-3 Practical Reference Electrodes

- ✓ Although the SHE has great fundamental importance, the difficulty in preparing the electrode surface and controlling the activities of the reactants make it so impractical that it is rarely used for routine measurements.
- ✓ 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. A thin coating of AgCl forms that adheres tightly to the wire.
- ✓ The wire is then immersed in a saturated solution of potassium chloride. A salt bridge connects the potassium chloride solution to the electrode system being studied.
- ✓ The potential of this electrode is about +0.22 V positive with respect to the SHE.
- ✓ The electrode half-reaction is $2\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Cl}^- + 2\text{Ag}(\text{s})$

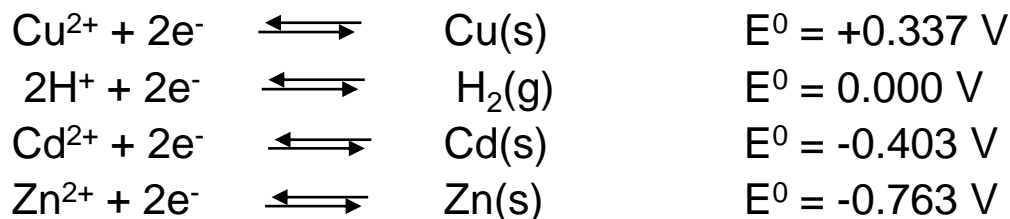
- ✓ A second widely used reference electrode is the **saturated calomel electrode (SCE)**, which consists of a pool of mercury in contact with a solution that is saturated with mercury(I) chloride (calomel) as well as potassium chloride.
- ✓ Platinum wire dipping in the mercury provides electrical contact to the other conductor, and a salt bridge to the second electrolyte completes the circuit.
- ✓ The potential of this reference is about 0.24 V positive. The electrode reaction is



22C-4 Definition of Electrode Potential

- ✓ An electrode potential is defined as the potential of a cell in which the electrode under investigation is the right hand electrode and the SHE is the left hand electrode.
- ✓ The electrode potential for the half-reaction $M^{2+} + 2e^- \rightleftharpoons M(s)$
- ✓ Here, the half-cell on the right consists of a strip of the metal M in contact with a solution of M^{2+} . The half-cell on the left 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.
- ✓ In this general example, we assume that the junction potentials across the salt bridge are zero.
- ✓ If we further 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.

- ✓ If M in the figure is Copper, Cadmium and Zinc, and their activity in the solution is 1.00, The standard electrode potentials can be arranged in the order



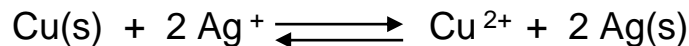
- ✓ The magnitudes of these standard electrode potentials show the relative strengths as electron acceptors; $Cu^{2+} > H^+ > Cd^{2+} > Zn^{2+}$. Oxidizing agent.

22C-5 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.
- The convention for cells is called the plus right rule. This rule implies that we always measure the cell potential by connecting the positive lead of the voltmeter to the right-hand electrode in the schematic or cell drawing.

- In the cell given like $\text{Cu} \mid \text{Cu}^{2+} (0.0200 \text{ M}) \parallel \text{Ag}^+ (0.0200 \text{ M}) \mid \text{Ag}$

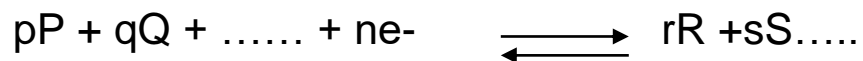
the direction of the overall process has Cu metal being oxidized to Cu^{2+} in the left hand compartment and Ag^+ being reduced to Ag metal in the right-hand compartment. In other words, the reaction for the process occurring in the cell is considered to be



- According to the IUPAC sign convention, as long as the liquid-junction potential is negligible or there is no liquid junction, we may write the cell potential E_{cell} as $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$ as given by Equation 22-12. Although we cannot determine absolute potentials of electrodes such as these, we can easily determine relative electrode potentials

22C-6 Effect of Activity on Electrode Potential

Let us consider the half-reaction



$$E = E^0 - \frac{0.0592}{n} \log \frac{(a_R)^r \cdot (a_S)^s \dots}{(a_P)^p \cdot (a_Q)^q \dots}$$

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), the collection of constants in front of the logarithm has units of joules per coulomb (volts). Therefore,

$$\begin{aligned} \frac{RT}{nF} &= \frac{8.316 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{n \times 96487 \text{ C mol}^{-1}} \\ &= \frac{2.568 \times 10^{-2} \text{ J C}^{-1}}{n} = \frac{2.568 \times 10^{-2}}{n} \text{ V} \end{aligned}$$

➤ When we convert from natural (ln) to base ten logarithms (log) by multiplying by 2.303, the previous equation can be written as

$$E = E^0 - \frac{0.0592}{n} \log \frac{(a_R)^r \cdot (a_S)^s \dots}{(a_P)^p \cdot (a_Q)^q \dots}$$

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

22C-7 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.

$$E = E^0 - \frac{0.0592}{n} \log \frac{(a_R)^r \cdot (a_S)^s \cdots}{(a_P)^p \cdot (a_Q)^q \cdots}$$

✓ 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.

✓ 4 facts regarding the standard electrode potential

(1) The electrode potential is temperature dependent; if it is to have significance, the temperature at which it is determined must be specified.

(2) The standard electrode potential is a relative quantity in the sense that it is really the potential of an electrochemical cell in which the left electrode is a carefully specified reference electrode—the SHE—whose potential is assigned a value of zero.

(3) The sign of a standard potential is identical with that of the conductor in the right-hand electrode in a galvanic cell, with the left electrode being the SHE.

(4) The standard potential is a measure of the driving force for a half-reaction. As such, it is independent of the notation used to express the half-cell process. Thus, although the potential for the process



- Standard electrode potentials have been tabulated for many half-reactions. Many have been determined directly from voltage measurements of cells with a SHE or other reference electrode. It is possible, however, to calculate E^0 values from equilibrium studies of oxidation-reduction systems and from thermochemical data relating to such reactions.
- The species in the upper part of the Table are most easily reduced, as indicated by the large positive E^0 values; they are therefore the most effective oxidizing agents.
- The half-cell rxns at the bottom of the table have little tendency to take place as reductions as written: they do tend to proceed as oxidations. The most effective reducing agents, then, are species that appear in the lower-right-hand side of the equations in the table.
- Zn is more easily oxidized than Cd, and when a piece of Zn is immersed in a solution of Cd ions, metallic Cd will deposit on the surface of the Zn, which will dissolve and produce Zn ions as long as there is an appreciable concent. of Cd ions in the solution
- in a solution containing an equilibrium mixture of iron(III), iodide, iron(II), and triiodide ions, we predict that iron(II) and triiodide will predominate.

TABLE 22-1 Standard Electrode Potentials

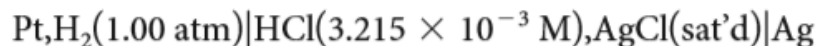
Reaction	E^0 at 25°C, V
$\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1.359
$\text{O}_2(g) + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.229
$\text{Br}_2(aq) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1.087
$\text{Br}_2(l) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1.065
$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}(s)$	+0.799
$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$	+0.771
$\text{I}_3^- + 2e^- \rightleftharpoons 3\text{I}^-$	+0.536
$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}(s)$	+0.337
$\text{Hg}_2\text{Cl}_2(s) + 2e^- \rightleftharpoons 2\text{Hg}(l) + 2\text{Cl}^-$	+0.268
$\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-$	+0.222
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + e^- \rightleftharpoons \text{Ag}(s) + 2\text{S}_2\text{O}_3^{2-}$	+0.010
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(g)$	0.000
$\text{AgI}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{I}^-$	-0.151
$\text{PbSO}_4(s) + 2e^- \rightleftharpoons \text{Pb}(s) + \text{SO}_4^{2-}$	-0.350
$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}(s)$	-0.403
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}(s)$	-0.763

22C-8 Measuring Electrode Potentials

- Although the SHE is the universal reference standard, the electrode, as described, is almost never used in the laboratory; it is a hypothetical electrode to which experimentally determined potentials can be referred only by suitable computation.
- The reason that the electrode, as defined, cannot be prepared is that we are unable to prepare a solution with a hydrogen ion activity of exactly unity.
- Neither the Debye-Hückel theory (see Appendix 2) nor any other theory of electrolyte solutions permits the determination of the activity coefficient of hydrogen ions in solutions with ionic strength approaching unity, as required by the definition of the SHE.
- Thus, the concentration of HCl or another acid required to give a hydrogen ion activity of unity cannot be calculated accurately.
- In spite of this limitation, data for more dilute solutions of acid, for which activity coefficients can be determined, can be used to compute hypothetical potentials at unit activity.
- The example that follows illustrates how standard potentials can be obtained in this way.

EXAMPLE 22-1

D. A. MacInnes⁸ found that a cell without liquid junction similar to that shown in Figure 22-2 has a potential of 0.52053 V. The cell is described by



Calculate the standard electrode potential for the half-reaction

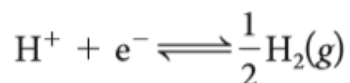


Solution

The electrode potential for the right-hand electrode is

$$\begin{aligned} E_{\text{right}} &= E_{\text{AgCl}}^0 - 0.0592 \log a_{\text{Cl}^-} \\ &= E_{\text{AgCl}}^0 - 0.0592 \log \gamma_{\text{Cl}^-} c_{\text{HCl}} \end{aligned}$$

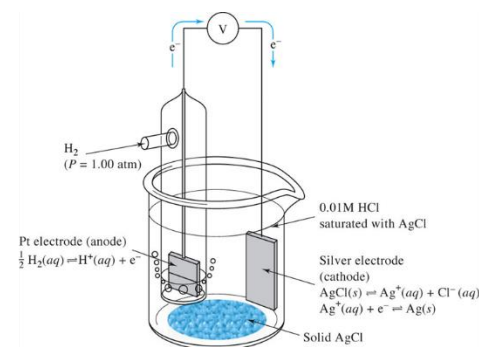
where γ_{Cl^-} is the activity coefficient of Cl^- . The left half-cell reaction is



and

$$\begin{aligned} E_{\text{left}} &= E_{\text{H}_2}^0 - \frac{0.0592}{1} \log \frac{P_{\text{H}_2}^{1/2}}{a_{\text{H}^+}} \\ &= E_{\text{H}_2}^0 - \frac{0.0592}{1} \log \frac{P_{\text{H}_2}^{1/2}}{\gamma_{\text{H}^+} c_{\text{HCl}}} \end{aligned}$$

The measured potential is the difference between these half-cell potentials (Equation 22-12):



$$\begin{aligned} E_{\text{cell}} &= (E_{\text{AgCl}}^0 - 0.0592 \log \gamma_{\text{Cl}^-} c_{\text{HCl}}) \\ &\quad - \left(0.000 - 0.0592 \log \frac{P_{\text{H}_2}^{1/2}}{\gamma_{\text{H}^+} c_{\text{HCl}}} \right) \end{aligned}$$

Combining the two logarithmic terms gives

$$E_{\text{cell}} = E_{\text{AgCl}}^0 - 0.0592 \log \frac{\gamma_{\text{H}^+} \gamma_{\text{Cl}^-} c_{\text{HCl}}^2}{P_{\text{H}_2}^{1/2}}$$

The activity coefficients for H^+ and Cl^- can be calculated from Equation a2-3 (Appendix 2) taking 3.215×10^{-3} for the ionic strength μ . These values are 0.945 and 0.939, respectively. If we substitute these activity coefficients and the experimental data into the previous equation and rearrange, we find

$$\begin{aligned} E_{\text{AgCl}}^0 &= 0.5203 \\ &\quad + 0.0592 \log \left[\frac{(3.215 \times 10^{-3})^2 (0.945)(0.939)}{1.00^{1/2}} \right] \\ &= 0.2223 \approx 0.222 \text{ V} \end{aligned}$$

(The mean for this and similar measurements at other concentrations of HCl was 0.222 V.)

22C-9 Calculating Half-Cell Potentials from E^0 values

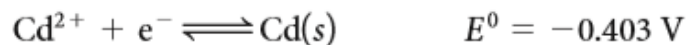
EXAMPLE 22-2

Nernst equation

What is the electrode potential for a half-cell consisting of a cadmium electrode immersed in a solution that is 0.0150 M in Cd^{2+} ?

Solution

From Table 22-1, we find



We will assume that $a_{\text{Cd}^{2+}} \approx [\text{Cd}^{2+}]$ and write

$$E_{\text{Cd}} = E_{\text{Cd}}^0 - \frac{0.0592}{2} \log \frac{1}{[\text{Cd}^{2+}]}$$

Substituting the Cd^{2+} concentration into this equation gives

$$E_{\text{Cd}} = -0.403 - \frac{0.0592}{2} \log \frac{1}{0.0150} = -0.457 \text{ V}$$

The sign for the potential calculated in Example 22-2 indicates the direction of the reaction when this half-cell is coupled with the SHE. The fact that it is negative shows that the reaction



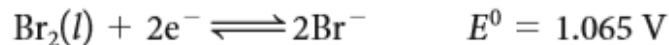
occurs spontaneously. Note that the calculated potential is a larger negative number than the standard electrode potential itself. This follows from mass-law considerations because the half-reaction, with 0.0150 M Cd^{2+} has less tendency to occur than it had with a Cd^{2+} activity of unity.

EXAMPLE 22-3

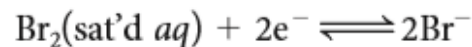
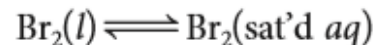
Calculate the potential for a platinum electrode immersed in a solution prepared by saturating a 0.0150 M solution of KBr with Br_2 .

Solution

The half-reaction is



Notice that the l following Br_2 indicates that the aqueous solution is saturated with *liquid* Br_2 . Thus, the overall process is the sum of the two equilibria



Assuming that $[\text{Br}^-] = a_{\text{Br}^-}$, the Nernst equation for the overall process is

$$E = 1.065 - \frac{0.0592}{2} \log \frac{[\text{Br}^-]^2}{1.00}$$

The activity of Br_2 in the pure liquid is constant and equal to 1.00 by definition. Thus,

$$\begin{aligned} E &= 1.065 - \frac{0.0592}{2} \log (0.0150)^2 \\ &= 1.173 \text{ V} \end{aligned}$$

22C-9 Calculating Half-Cell Potentials from E^0 values

EXAMPLE 22-4

Calculate the potential for a platinum electrode immersed in a solution that is 0.0150 M in KBr and 1.00×10^{-3} M in Br_2 .

›Solution

In this example, the half-reaction used in the preceding example *does not apply because the solution is no longer saturated in Br_2* . Table 22-1, however, contains the half-reaction



The *aq* implies that all of the Br_2 present is in solution and that 1.087 V is the electrode potential for the half-reaction when the Br^- and $\text{Br}_2(aq)$ activities are 1.00 mol/L. It turns out, however, that the solubility of Br_2 in water at 25°C is only about 0.18 mol/L. Therefore, the recorded potential of 1.087 V is based on a hypothetical system that cannot be achieved experimentally. Nevertheless, this potential is useful because it provides the means by which potentials for undersaturated systems can be calculated. Thus, if we assume that activities of solutes are equal to their molar concentrations, we obtain

$$\begin{aligned} E &= 1.087 - \frac{0.0592}{2} \log \frac{[\text{Br}^-]^2}{[\text{Br}_2]} \\ E &= 1.087 - \frac{0.0592}{2} \log \frac{(1.50 \times 10^{-2})^2}{1.00 \times 10^{-3}} \\ &= 1.106 \text{ V} \end{aligned}$$

In this case, the Br_2 activity is 1.00×10^{-3} rather than 1.00, as was the situation when the solution was saturated and excess $\text{Br}_2(l)$ was present.

EXAMPLE 22-5
22C-10 Electrode Potentials in the Presence of Precipitate

Calculate the potential of a silver electrode in a solution that is saturated with silver iodide and has an iodide ion activity of (a) exactly 0.001 and (b) exactly 1.00 (K_{sp} for AgI = 8.3×10^{-17}).



$$E = +0.799 - 0.0592 \log \frac{1}{a_{\text{Ag}^+}}$$

Solution

We may calculate a_{Ag^+} from the solubility-product constant. Thus,

$$a_{\text{Ag}^+} = \frac{K_{sp}}{a_{\text{I}^-}}$$

Substituting this expression into the Nernst equation gives

$$E = +0.799 - \frac{0.0592}{1} \log \frac{a_{\text{I}^-}}{K_{sp}}$$

This equation may be rewritten as

$$E = +0.799 + 0.0592 \log K_{sp} - 0.0592 \log a_{\text{I}^-} \quad (22-14)$$

(a) If we substitute 0.001 for a_{I^-} and use 8.3×10^{-17} for K_{sp} , the solubility product for AgI at 25.0°C, we obtain

$$\begin{aligned} E &= +0.799 + 0.0592 \log 8.3 \times 10^{-17} \\ &\quad - 0.0592 + \log 0.001 = 0.025 \text{ V} \end{aligned}$$

(b) for $a_{\text{I}^-} = 1.00$, $E = -0.153 \text{ V}$

This example shows that the half-cell potential for the reduction of silver ions becomes smaller and eventually negative as the concentration of iodide ion increases. Qualitatively, this is what we expect because decreases in the silver ion concentration decreases the tendency for their reduction.

Equation 22-14 relates the potential of a silver electrode to the iodide ion activity of a solution that is also saturated with silver iodide. *When the iodide ion activity is unity*, the potential is the sum of two constants; it is thus the standard electrode potential for the half-reaction



where

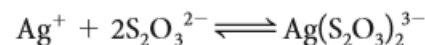
$$E_{\text{AgI}}^0 = +0.799 + 0.0592 \log K_{sp}$$

The Nernst relationship for the silver electrode in a solution *saturated with silver iodide* can then be written as

$$E = E^0 - 0.0592 \log a_{\text{I}^-} = -0.1513 - 0.0592 \log a_{\text{I}^-}$$

Thus, when in contact with a solution saturated with silver iodide, the potential of a silver electrode can be described *either* in terms of the silver ion activity (with the standard electrode potential for the simple silver half-reaction) *or* in terms of the iodide ion activity (with the standard electrode potential for the silver–silver iodide half-reaction). The silver–silver iodide half-reaction is usually more convenient.

The potential of a silver electrode in a solution containing an ion that forms a soluble complex with silver ion can be handled in a way analogous to the treatment above. For example, in a solution containing thiosulfate and silver ions, complex formation occurs:



$$K_f = \frac{a_{\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}}}{a_{\text{Ag}^+} \cdot (a_{\text{S}_2\text{O}_3^{2-}})^2}$$

where K_f is the formation constant for the complex. The half-reaction for a silver electrode in such a solution can be written as



The standard electrode potential for this half-reaction is the electrode potential when both the complex and the complexing

22C-11 Limitations to the Use of Standard Electrode Potentials

a.) E° based on unit activities not concentrations

- activity = concentration, only in dilute solutions
- at higher concentrations need to determine and use activity

$$a_X = \gamma_X[X]$$

- example:

- neglecting activities $\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+}$ $E^\circ = +0.771 \text{ V}$

- but at 1M acid conc. $\gamma_X < 1$ $E^\circ = +0.732 \text{ V}$,

- problem if γ_X not known from calculations or previous experimental studies

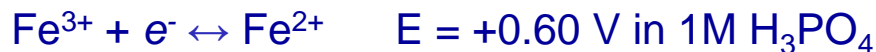
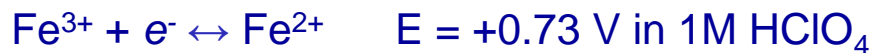
$$-\log \gamma_A = \frac{0.509 Z_A^2 \sqrt{\mu}}{1 + 3.28 \alpha_A \sqrt{\mu}}$$

Debye-Huckel Equation

b.) Side Reactions can Affect E° :

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

- example:



- *reason*: Fe^{2+} & Fe^{3+} form different complexes with Cl^- & PO_4^- that affects net activity of Fe^{2+} and Fe^{3+} in solution

b.) Use of Formal Potentials, E° , in place of the standard electrode potential

- to compensate for problems with E° in using activity and with side-reactions
- Formal potential of a system is the potential of the half-cell with respect to the SHE, when the concentrations of reactants and products are 1 M and the concentrations of any other constituents of the solution are carefully specified.
- e.g. HCl vs. HClO₄ as acid for the reduction of iron(III)
 - gives better agreement than E° with experimental data and Nernst Equation
 - conditions need to be similar to conditions where E° was measured
 - Appendix 3 contains selected formal potentials as well as standard potentials

c.) Reaction Rates:

- some E° $\frac{1}{2}$ reactions listed in tables have been determined by calculations from *equilibrium* measurements rather than actual measurements of the $\frac{1}{2}$ cell in an electrode system.
- For some half- reactions, no suitable electrode is known. For example, the standard electrode potential for the process



was determined indirectly.

- *problem*- reaction is slow and difficult to see in practice
 - thermodynamics vs. kinetics
 - no suitable electrode
- In spite of the absence of direct measurements, the tabulated potential is useful for computational purposes.

22D 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.

✓ These calculated potentials refer to cells in which there is no current.

✓ Furthermore, these potentials do not take into account junction potentials within the cell.

Normally, junction potentials can be made small enough to be neglected without serious error.

✓ We calculate the voltage of a cell from the difference betw. two half-cell potentials

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

✓ Consider a hypothetical cell $\text{Zn} \mid \text{ZnSO}_4(a_{\text{Zn}^{2+}} = 1.00) \parallel \text{CuSO}_4(a_{\text{Cu}^{2+}} = 1.00) \mid \text{Cu}$

✓ Because the activities of the two ions are both 1.00, the standard potentials are also the

electrode potentials. Thus, $E_{\text{cell}} = +0.337 - (-0.763) = +1.100 \text{ V}$

The positive sign for the cell potential indicates that the reaction



✓ If the preceding cell is written in the reverse sense,



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

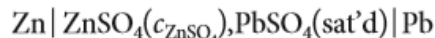
$$E_{\text{cell}} = -0.763 - (+0.337) = -1.100 \text{ V}$$

The negative sign indicates the nonspontaneity of the reaction

The application of an external potential greater than 1.100 V is required to cause this reaction to occur.

EXAMPLE 22-6

Calculate potentials for the following cell using (a) concentrations and (b) activities:



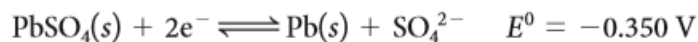
where $c_{\text{ZnSO}_4} = 5.00 \times 10^{-4}$, 2.00×10^{-3} , 1.00×10^{-2} , 2.00×10^{-2} , and 5.00×10^{-2} .

Solution

(a) In a neutral solution, little HSO_4^- will be formed; thus, we may assume that

$$[\text{SO}_4^{2-}] = c_{\text{ZnSO}_4} = 5.00 \times 10^{-4}$$

The half-reactions and standard potentials are



The potential of the lead electrode is given by

$$\begin{aligned} E_{\text{Pb}} &= -0.350 - \frac{0.0592}{2} \log 5.00 \times 10^{-4} \\ &= -0.252 \text{ V} \end{aligned}$$

The zinc ion concentration is also 5.00×10^{-4} and

$$\begin{aligned} E_{\text{Zn}} &= -0.763 - \frac{0.0592}{2} \log \frac{1}{5.00 \times 10^{-4}} \\ &= -0.860 \text{ V} \end{aligned}$$

Because the Pb electrode is specified as the right-hand electrode,

$$E_{\text{cell}} = -0.252 \text{ V} - (-0.860 \text{ V}) = 0.608 \text{ V}$$

Note that the value calculated using concentrations (0.608 V) is about 1% different from this value.

(b) To calculate activity coefficients for Zn^{2+} and SO_4^{2-} , we must first find the ionic strength using Equation a2-3 (Appendix 2). We assume that the concentrations of Pb^{2+} , H^+ , and OH^- are negligible compared to the concentrations of Zn^{2+} and SO_4^{2-} . Thus, the ionic strength is

$$\begin{aligned} \mu &= \frac{1}{2} [5.00 \times 10^{-4} \times (2)^2 + 5.00 \times 10^{-4} \times (2)^2] \\ &= 2.00 \times 10^{-3} \end{aligned}$$

In Table a2-1, we find for SO_4^{2-} , $\alpha_A = 0.4$, and for Zn^{2+} , $\alpha_A = 0.6$. Substituting these values into Equation a2-3 gives for sulfate ion

$$\begin{aligned} -\log \gamma_{\text{SO}_4^{2-}} &= \frac{0.0509 \times 2^2 \times \sqrt{2.00 \times 10^{-3}}}{1 + 3.28 \times 0.4 \times \sqrt{2.00 \times 10^{-3}}} \\ &= 0.859 \times 10^{-2} \end{aligned}$$

$$\gamma_{\text{SO}_4^{2-}} = 0.820$$

$$\begin{aligned} a_{\text{SO}_4^{2-}} &= 0.820 \times 5.00 \times 10^{-4} \\ &= 4.10 \times 10^{-4} \end{aligned}$$

Repeating the calculations using $\alpha_A = 0.6$ for Zn^{2+} yields

$$\gamma_{\text{Zn}^{2+}} = 0.825$$

$$a_{\text{Zn}^{2+}} = 4.13 \times 10^{-4}$$

The Nernst equation for the Pb electrode now becomes

$$\begin{aligned} E_{\text{Pb}} &= -0.350 - \frac{0.0592}{2} \times \log 4.10 \times 10^{-4} \\ &= -0.250 \end{aligned}$$

For the zinc electrode

$$\begin{aligned} E_{\text{Zn}} &= -0.763 - \frac{0.0592}{2} \times \log \frac{1}{4.13 \times 10^{-4}} \\ &= -0.863 \end{aligned}$$

and

$$E_{\text{cell}} = -0.250 - (-0.863) = 0.613 \text{ V}$$

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.
- ✓ When there is a direct current in an electrochemical cell, the measured cell potential normally departs from the thermodynamic potential calculated. This departure can be traced to a number of phenomena, including:
 - ✓ **ohmic potential** and
 - ✓ **several polarization effects**, such as :
 - ✓ charge-transfer overvoltage,
 - ✓ reaction overvoltage,
 - ✓ 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.*

$$E_{\text{applied}} = E_{\text{cathode}} - E_{\text{anode}} - IR \quad (22-16)$$

EXAMPLE 22-7

The following cell has a resistance of 4.00Ω . Calculate its potential when it is producing a current of 0.100 A .



➤ Solution

By substituting the standard potentials and concentrations into the Nernst equation, we find that the electrode potential for the Cu electrode is 0.278 V , and for the Cd electrode it is -0.462 V . Thus, the thermodynamic cell potential is

$$E = E_{\text{Cu}} - E_{\text{Cd}} = 0.278 - (-0.462) = 0.740 \text{ V}$$

and the potential to yield the desired current is

$$\begin{aligned} E_{\text{cell}} &= 0.740 \text{ V} - IR \\ &= 0.740 \text{ V} - (0.100 \text{ A} \times 4.00 \Omega) = 0.340 \text{ V} \end{aligned}$$

EXAMPLE 22-8

Calculate the potential required to generate a current of 0.100 A in the reverse direction in the cell shown in Example 22-7.

➤ Solution

$$\begin{aligned} E &= E_{\text{Cd}} - E_{\text{Cu}} \\ &= -0.462 \text{ V} - 0.278 \text{ V} = -0.740 \text{ V} \\ E_{\text{cell}} &= E - IR \\ &= -0.740 \text{ V} - (0.100 \text{ A} \times 4.00 \Omega) = -1.140 \text{ V} \end{aligned}$$

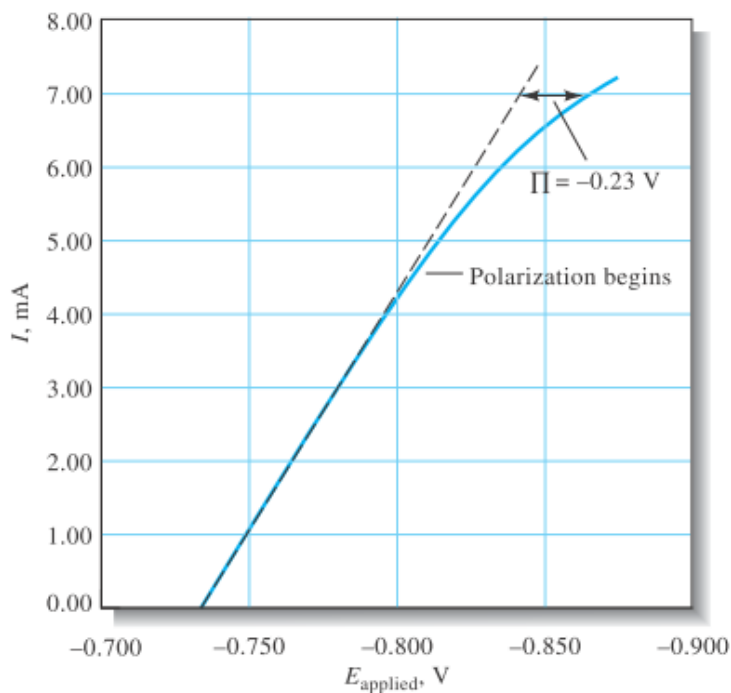
In this example, an external potential greater than 1.140 V is needed to cause Cd^{2+} to deposit and Cu to dissolve at a rate required for a current of 0.100 A .

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 $E_{\text{applied}} = E_{\text{cathode}} - E_{\text{anode}} - IR$ 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/overpotential, which is symbolized by Π .

$$E_{\text{applied}} = E_{\text{cell}} - IR - \Pi$$

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.

Ideal Polarized and Nonpolarized Electrodes and Cells

- The ideal polarized electrode is one in which current remains constant and independent of potential over a wide range. Figure 22-6a and b is a current-voltage curve for an electrode that is ideally polarized and non-polarized in the region between A and B. .

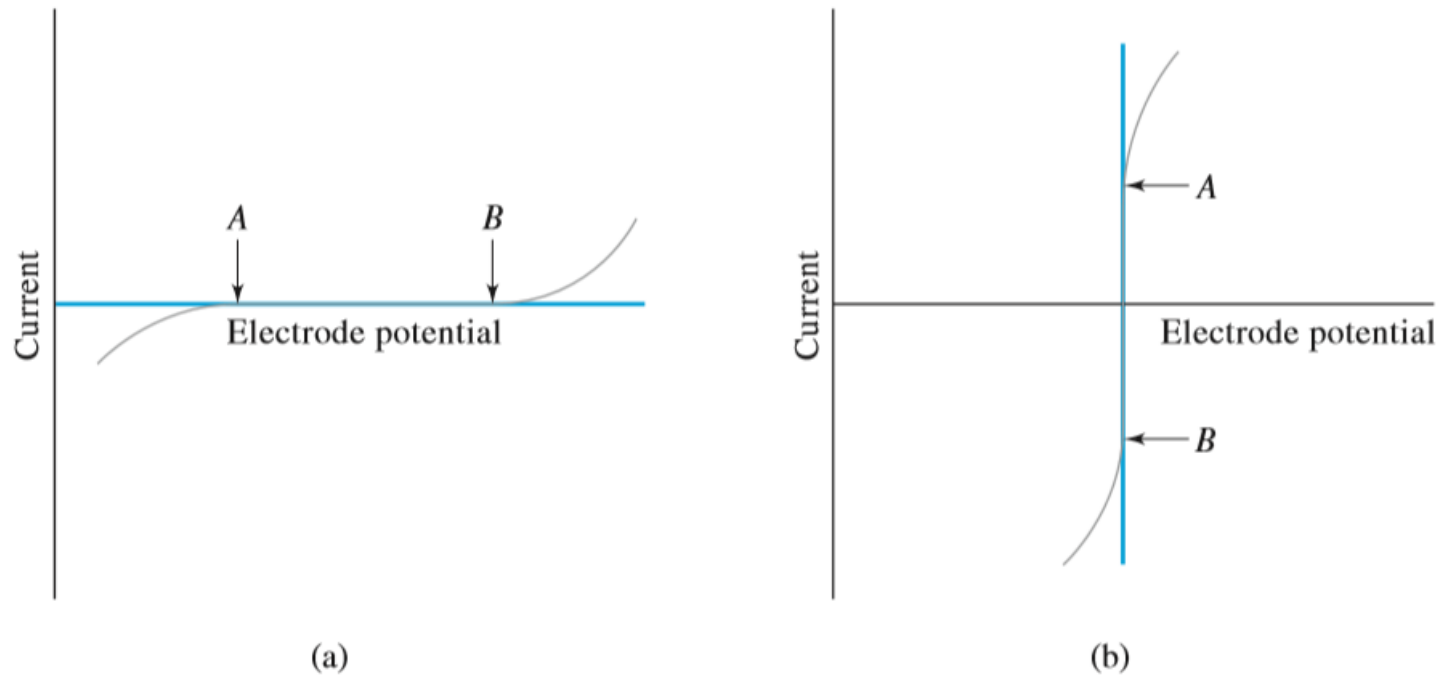


FIGURE 22-6 Current-voltage curves in blue for an ideal (a) polarized and (b) nonpolarized electrode. Gray lines show departure from ideal behavior by real electrodes.

Sources of Polarization in Electrolytic Cells

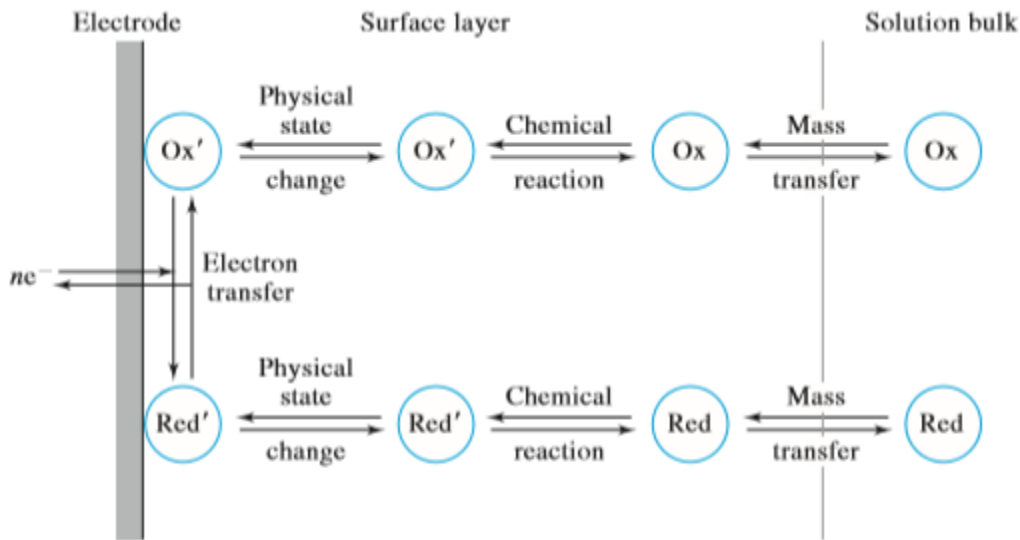


FIGURE 22-8 Steps in the reaction $\text{Ox} + ne^- \rightleftharpoons \text{Red}$ at an electrode. Note that the surface layer is only a few molecules thick. (Adapted from A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, 2nd ed., p. 23, New York: Wiley, 2001. Reprinted by permission of John Wiley & Sons, Inc.)

- ✓ three regions of a half-cell in an electrolytic cell where polarization can occur.
- ✓ These regions include the
 - 1) electrode itself,
 - 2) a surface film of solution immediately adjacent to the electrode, and
 - 3) the bulk of the solution.

For this half-cell, the overall electrode reaction is $\text{Ox} + ne^- \longrightarrow \text{Red}$

Polarization phenomena can be divided into two categories:

- a) concentration polarization and b) reaction 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. 46

If the rate of formation or decomposition of the intermediate limits the current, **reaction polarization** occurs. In some instances, the rate of a physical process such as adsorption, desorption, or crystallization limits the current. In these cases, adsorption, desorption, or crystallization polarization occurs. Finally, when the current is limited by a slow rate of electron transfer from the electrode to the oxidized species in the surface film or from the reduced species to the electrode, we have charge-transfer polarization. It is not unusual to find several types of polarization occurring simultaneously.

Overvoltage

The degree of polarization of an electrode in an electrolytic cell is measured by the overvoltage, or overpotential, η , which is the difference between the actual electrode potential E and the thermodynamic, or equilibrium, potential E_{eq} . That is,

$$\eta = E - E_{\text{eq}} \quad (22-17)$$

In this expression, η is the additional potential beyond the thermodynamic value needed to cause the reaction to occur at an appreciable rate. For cathodic reactions where E_{eq} is negative, E must be more negative than E_{eq} , and η is negative. For anodic reactions where E_{eq} is positive, E must be more positive than E_{eq} , and η is positive.

22E-3 Mechanism of Mass Transport

- ✓ 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.

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_0 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.

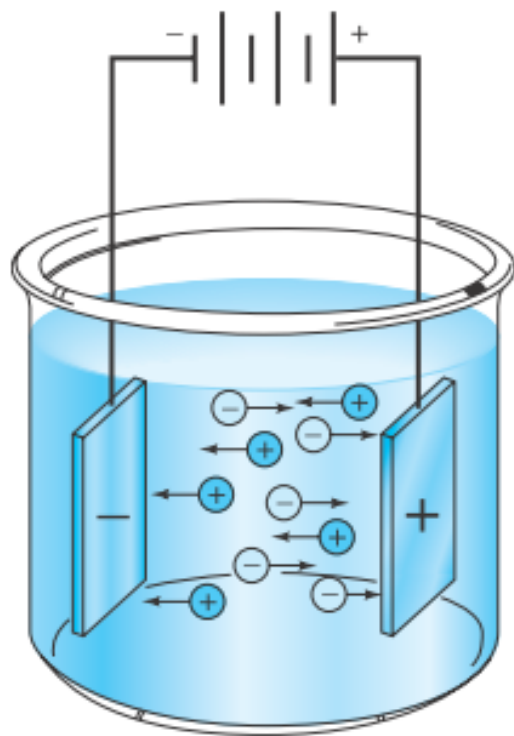


Figure 22-5 The motion of ions through a solution because of the electrostatic attraction between the ions and the electrodes is called migration.

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.

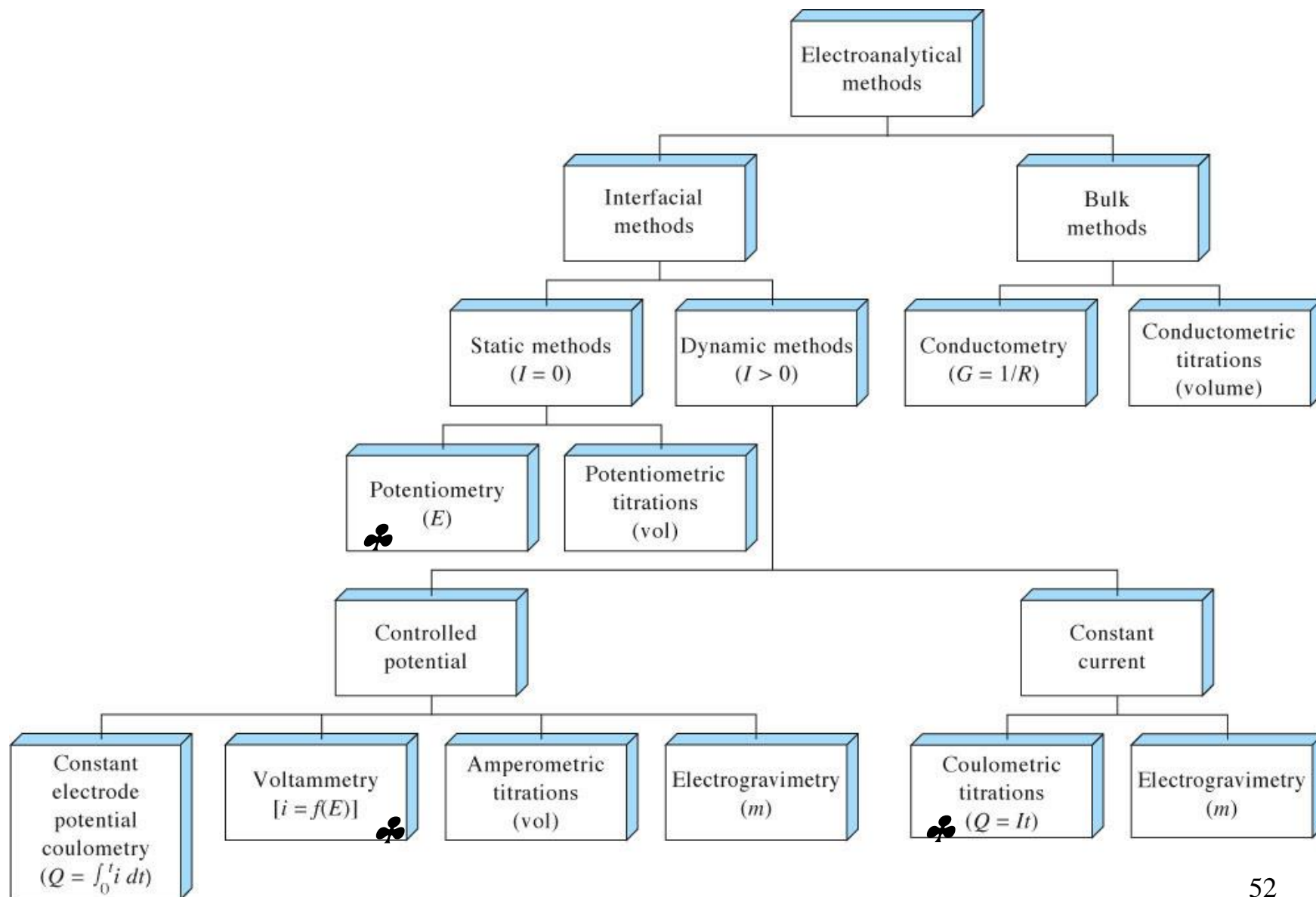
Because of concentration polarization, a larger potential must be applied to an electrolytic cell than the value predicted from the thermodynamic potential and the *IR drop*.

22E-4 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.

22F Types of Electroanalytical Methods



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