



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

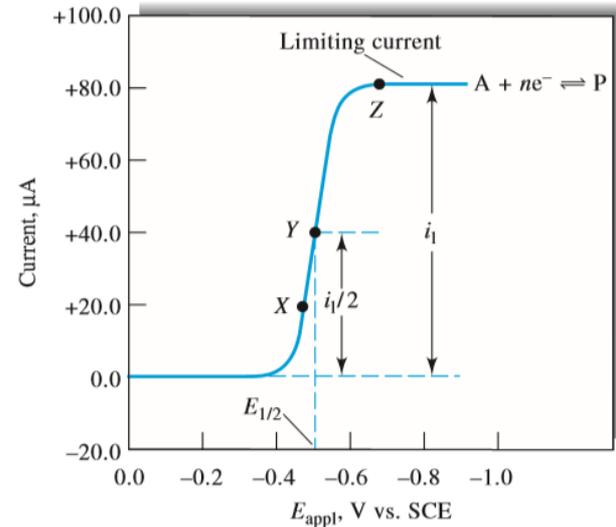
Fundamentals of Analytical Chemistry 9e by Douglas A. Skoog, 2013.

Chapter 25

Voltammetry

Introduction To Voltammetry:

- Voltammetry comprises a group of electroanalytical methods in which information about the analyte is obtained by measuring *current as a function of applied potential*
- The change in current with the varying voltage gives the plot and is known as *voltammogram*
- Voltammetric measurements occur under conditions that promote *polarization* of an indicator(working) electrode.
- In a closely related technique, *amperometry*, current proportional to analyte concentration is monitored at a *fixed potential*.
- Generally, to enhance polarization, working electrodes in voltammetry and amperometry have surface areas of a few square millimeters at the most and, in some applications, a few square micrometers or less.



POTENTIOMETRY

* potentiometric measurements are made at currents that approach zero and where polarization is absent.

VOLTAMMETRY

* Voltammetry is based on the measurement of the current that develops in an electrochemical cell under conditions where concentration polarization exists

* there is minimal consumption of the analyte

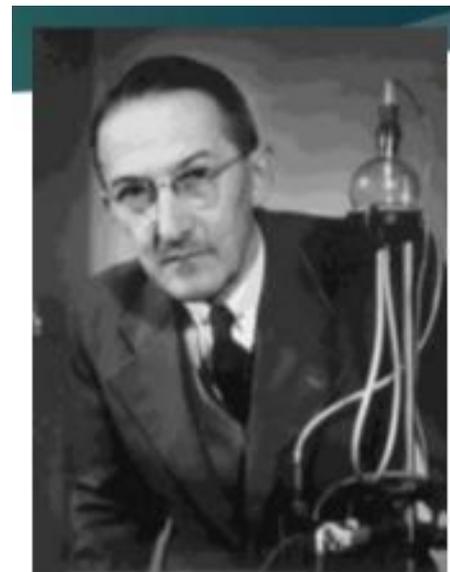
COULOMETRY

* measures are taken to minimize or compensate for the effects of concentration polarization.

* essentially all of the analyte is converted to another state.

HISTORY:

- The field of voltammetry developed from *polarography*, which is a particular type of voltammetry invented by the Czechoslovakian chemist Jaroslav Heyrovsky in the early 1920s.
- Polarography differs from other types of voltammetry in that the working electrode is the unique dropping mercury electrode.
- At one time, polarography was an important tool used by chemists for the determination of inorganic ions and certain organic species in aqueous solution.
- In the late 1950s and the 1960s, however, many of these analytical applications were replaced by spectroscopic methods. As a result, polarography became a less-important method of analysis .



HISTORY

- Polarographic methods has steadily declined as a result of concerns about the use of large amounts of mercury (toxic) in the laboratory as well as in the environment. Also somewhat cumbersome nature of the apparatus, and broad availability of faster and more convenient (spectroscopic) methods are the reasons.
- For these reasons, we will discuss polarography only briefly and, instead, refer to the many sources that are available on the subject.
- Although polarography declined in importance, voltammetry and amperometry at working electrodes other than the dropping mercury electrode continues to be an excellent tool in diverse areas of chemistry, biochemistry, materials science and engineering, and the environmental sciences for studying
 - Oxidation-reduction processes
 - adsorption processes on surfaces and
 - electron transfer mechanism

25A EXCITATION SIGNALS IN VOLTAMMETRY

In voltammetry, a variable potential excitation signal is impressed on a working electrode in an electrochemical cell

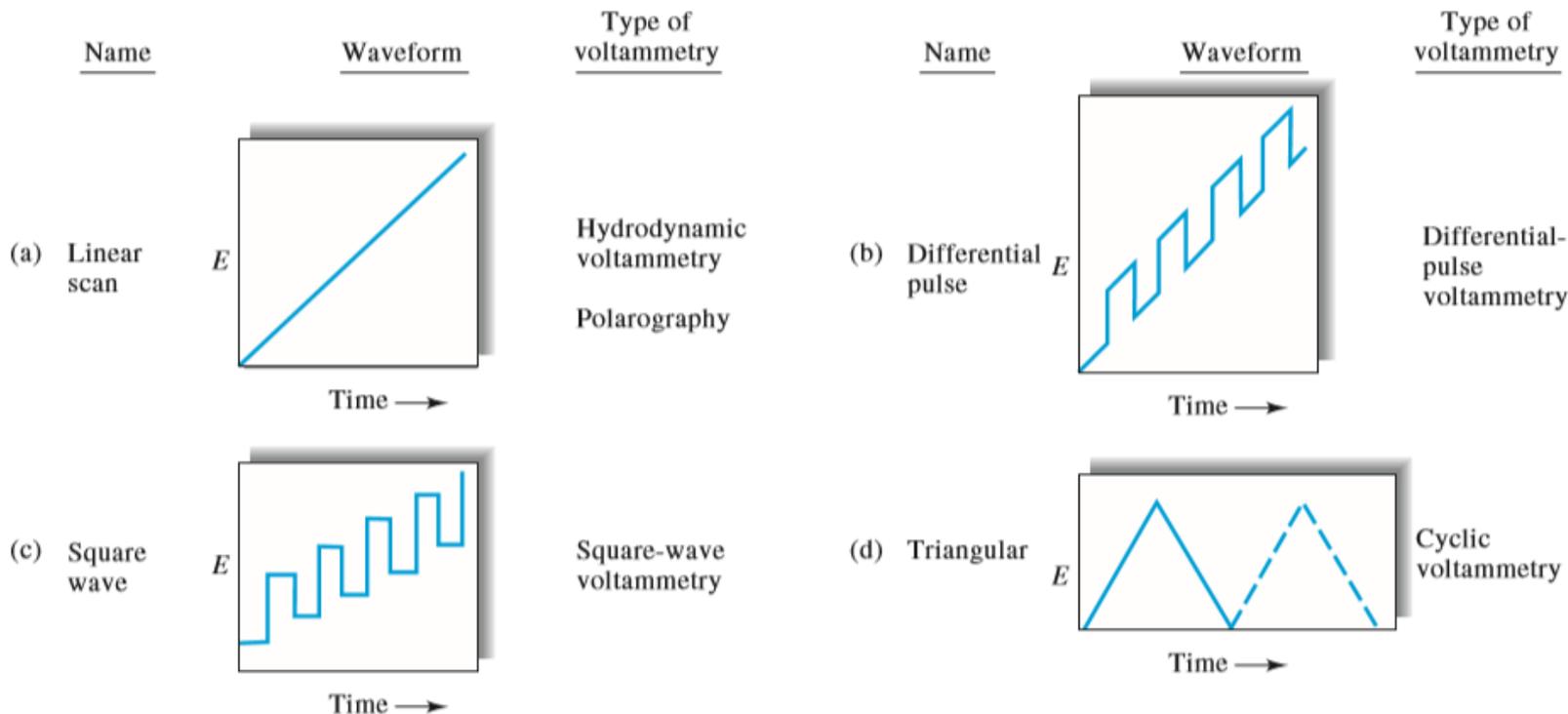


FIGURE 25-1 Voltage versus time excitation signals used in voltammetry.

The classical voltammetric excitation signal is the linear scan shown in Figure 25-1a, in which the voltage applied to the cell increases linearly as a function of time. Two pulse excitation signals are shown in Figure 25-1b and c. Currents are measured at various times during the lifetime of these pulses. With the triangular waveform shown in Figure 25-1d, the potential is cycled between two values, first increasing linearly to a maximum and then decreasing linearly with the same slope to its original value.

25B VOLTAMMETRIC INSTRUMENTATION

➤ The cell is made up of 3 electrodes immersed in a solution containing the analyte and also an excess of a nonreactive electrolyte called a

supporting electrolyte: alkali metal salt

– No reaction at the E region – Reduce the effect of migration – Lower R of the solution

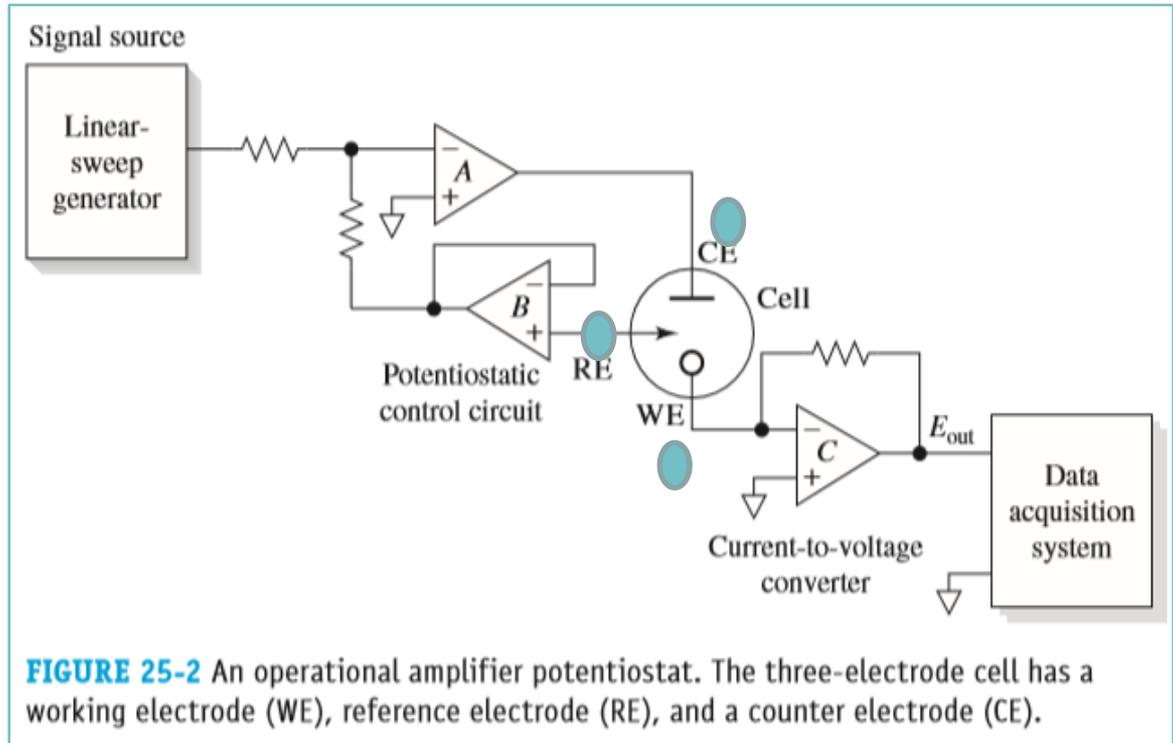
➤ working electrode (*WE*), whose potential is varied linearly with time. Its dimensions are kept small to enhance its tendency to become polarized.

➤ reference electrode (*RE*; commonly a saturated calomel or a silver–silver chloride electrode) whose potential remains constant throughout the experiment.

➤ counter electrode (*CE*), a coil of platinum wire that serves merely to carry the current flowing through the cell. Simply conducts electricity from the signal source through the solution to the working electrode.

➤ The signal source is a linear-sweep (linear-scan) generator

➤ The electrical resistance of the control circuit containing the ref. electrode is so large $>10^{11}\Omega$ that it draws essentially no current. Thus, the the entire current from the source is carried from the counter electrode to the working electrode



25B-1 WORKING ELECTRODES

- Ranges from small mercury drop to flat platinum disc.
- Other commonly used electrode materials gold, platinum and glassy carbon.
- Depending on the choice of working electrode, the type of voltammetry is decided.
 - Dropping Mercury Electrode(DME) in Polarography
 - Platinum electrode in Cyclic Voltammetry
 - Glassy Carbon electrode in Linear Sweep Voltammetry.

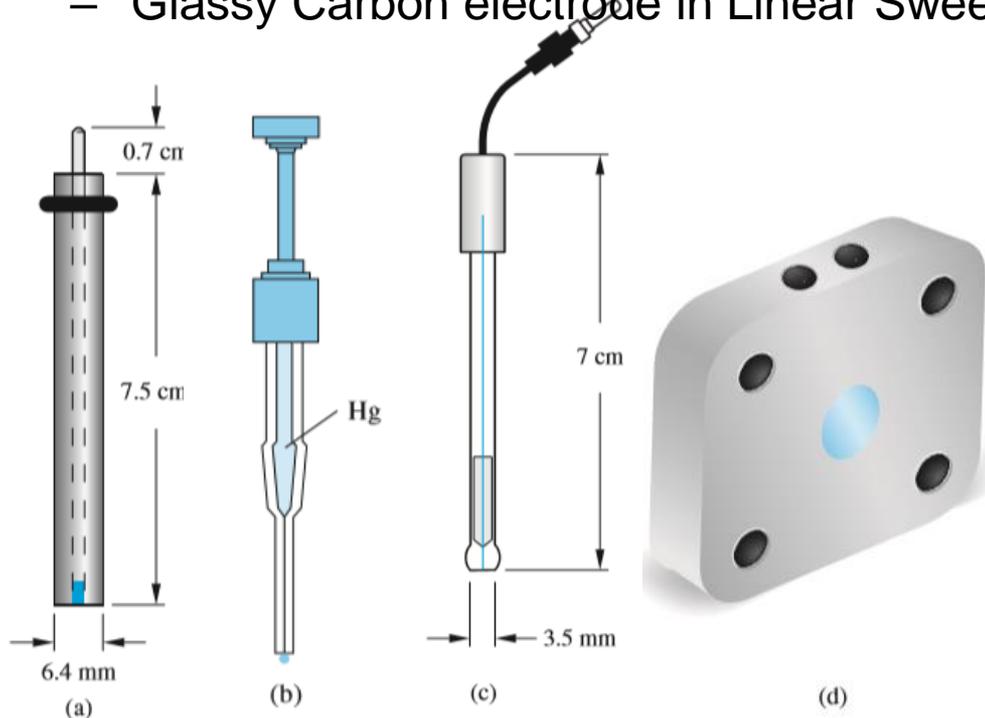


Figure 25-3 Some common types of commercial voltammetric electrodes (a) a disk electrode; (b) hanging mercury drop electrode (HMDE); (c) a microelectrode; (d) a sandwich-type flow electrode.

25B-2 MODIFIED ELECTRODES

- Chemical modification of various conductive substrates.
 - Irreversibly adsorbing substances
 - oxidation of metal or C electrode surface (O- or –OH)
 - electrodeposition
 - Covalent bonding of components :
 - » like SAM of thiols with amine or carboxyl group on the other end
 - » Organosilanes or amines –
- Coating of polymer films
- -Dip coating, spin coating

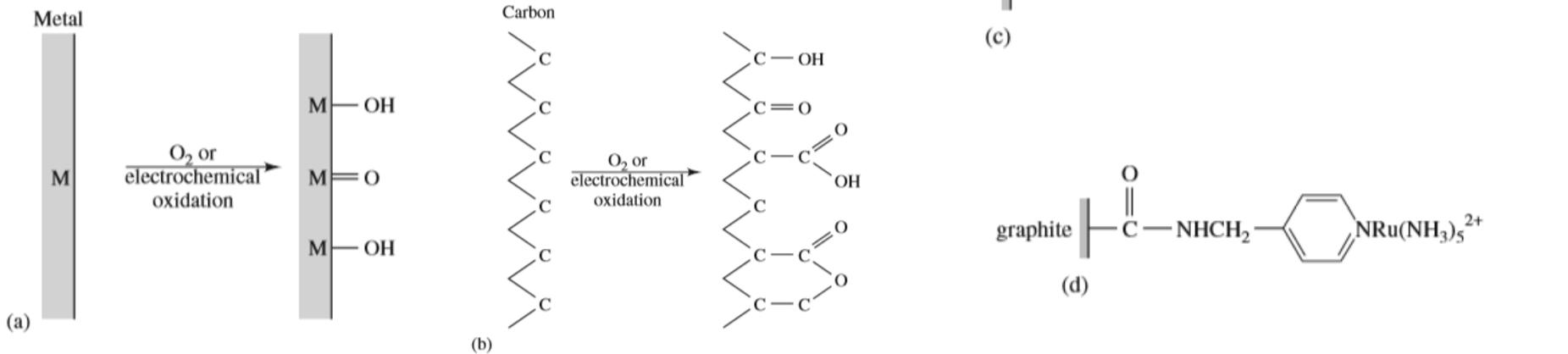


Figure 25-5 Functional groups formed on (a) a metal or (b) a carbon surface by oxidation. (c) a linking agent such as the organosilane shown is often bonded to the functionalized surface. Reactive components, such as ferrocenes, viologens, and metal bipyridine complexes, are then attached to form the modified surfaces. A Pt electrode is shown with a ferrocene attached. (d), a graphite electrode is shown with attached py-ru(NH₃)₅.

25B-3 VOLTAMMOGRAMS



-Here, the working electrode is assumed to be connected to the negative terminal of the linear-scan generator so that the applied potentials are given a negative sign as shown.

-By convention, cathodic currents are taken to be positive, whereas anodic currents are given a negative sign.

- Linear-sweep voltammograms generally have a *sigmoid* shape and are called *voltammetric waves*. The constant current beyond the steep rise is called the *diffusion-limited current*, or simply the *limiting current*, i_l . $i_l = k \cdot c_A$

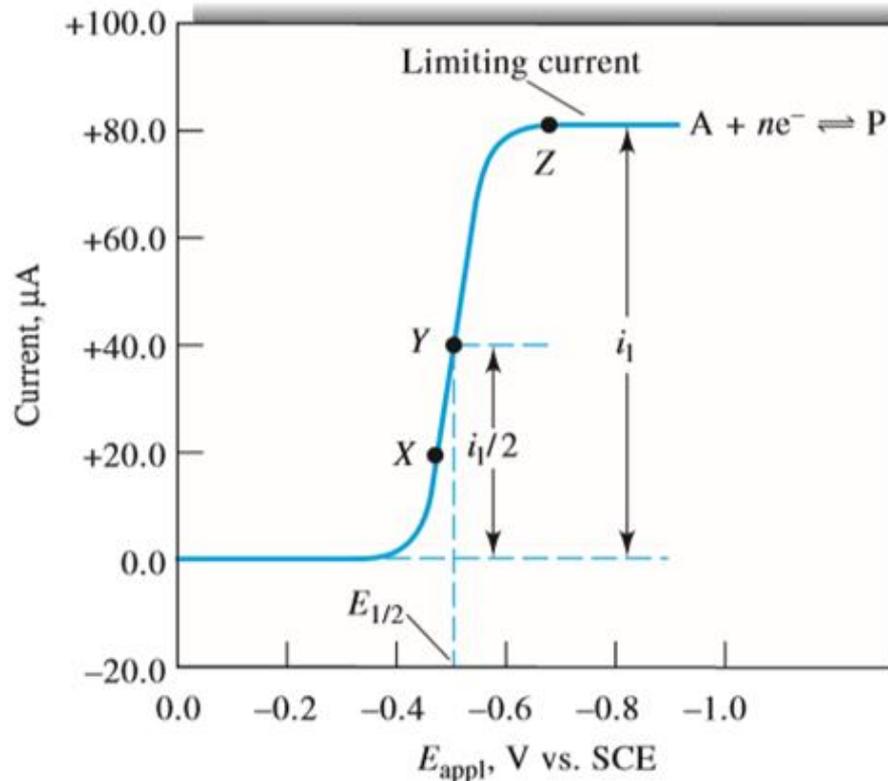


Figure 25-6 linear-sweep voltammogram for the reduction of a hypothetical species A to give a product P.

- Quantitative linear-scan voltammetry relies on this relationship.

- The potential at which the current is equal to one half the limiting current is called the half-wave potential and given the symbol $E_{1/2}$ and is often used for qualitative analysis.

- Linear-scan voltammetry in which the solution or the electrode is in constant motion is called *hydrodynamic voltammetry*.

25C Hydrodynamic Voltammetry

• Hydrodynamic voltammetry is performed in several ways. In one method the solution is stirred vigorously while it is in contact with a fixed working electrode. In this typical cell, Figure 25-8, stirring is accomplished with an ordinary magnetic stirrer. Another approach is to rotate the working electrode at a constant high speed in the solution to provide the stirring action

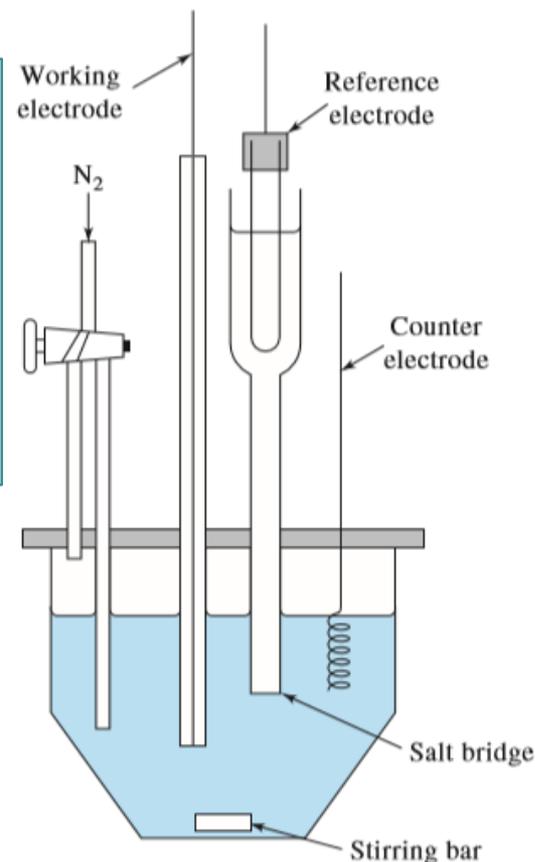


FIGURE 25-8 A three-electrode cell for hydrodynamic voltammetry.

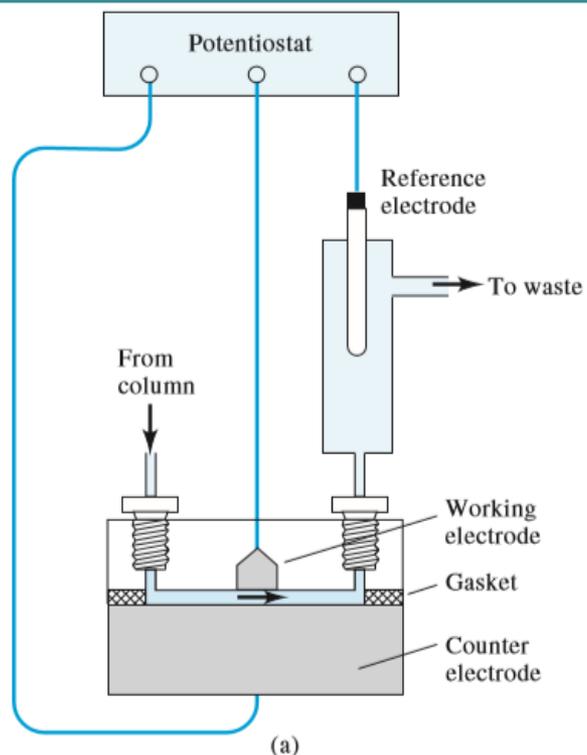


FIGURE 25-17 (a) A schematic of a voltammetric system for detecting electroactive species as they elute from a column. The cell volume is determined by the thickness of the gasket.

- Still another way of doing hydrodynamic voltammetry is to pass an analyte solution through a tube fitted with a working electrode. The last technique is widely used for detecting oxidizable or reducible analytes as they exit from a liquid chromatographic column or a flow-injection manifold.

25C Hydrodynamic Voltammetry

- Ch-22, During an electrolysis, reactant is carried to the surface of an electrode by three mechanisms:
 - migration** under the influence of an electric field,
 - convection** resulting from stirring or vibration, and
 - diffusion** due to concentration differences between the film of liquid at the electrode surface and the bulk of the solution.
- In voltammetry, we attempt to minimize the effect of migration by introducing an excess of an inactive **supporting electrolyte**.
- When the concentration of supporting electrolyte exceeds that of the analyte by 50- to 100-fold, the fraction of the total current carried by the analyte approaches zero. As a result, the rate of migration of the analyte toward the electrode of opposite charge becomes essentially independent of applied potential.

25C-1 Concentration Profiles at electrode Surfaces



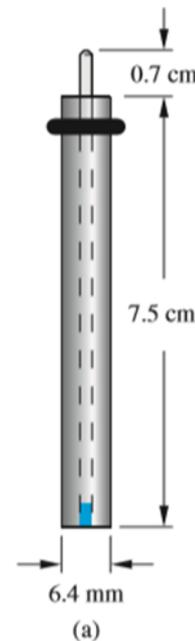
$$E_{\text{appl}} = E_A^0 - \frac{0.0592}{n} \log \frac{c_P^0}{c_A^0} - E_{\text{ref}}$$

- We will assume that the initial concentration of A is c_A and that of the product P is zero.
- We also assume that the reduction reaction is rapid and reversible so that the concentrations of A and P in the film of solution immediately adjacent to the electrode is given at any instant by the Nernst equation:

- the concentration of A in the bulk of the solution c_A is unchanged by the electrolysis
- the concentration of P in the bulk of the solution c_P continues to be, for all practical purposes, zero ($c_P \sim 0$).

➤ Profiles for Planar Electrodes in Unstirred Solutions

- in the absence of convection—that is, in an unstirred solution- mass transport of the analyte to the electrode surface occurs by **diffusion** alone.



➤ Profiles for Planar Electrodes in Unstirred Solutionscont'd

Let us assume that a potential step of magnitude E_{appl} is applied to the working electrode for a period of time t as shown in Figure 25-9a. Let us further assume that E_{appl} is large enough that the ratio $c_{\text{P}}^0 / c_{\text{A}}^0$ is 1000 or greater. Under this condition, the concentration of A at the electrode surface is, for all practical purposes, immediately reduced to zero ($c_{\text{A}}^0 \rightarrow 0$). The current response to this step-excitation signal is shown in Figure 25-9b.

$$E_{\text{appl}} = E_{\text{A}}^0 - \frac{0.0592}{n} \log \frac{c_{\text{P}}^0}{c_{\text{A}}^0} - E_{\text{ref}}$$

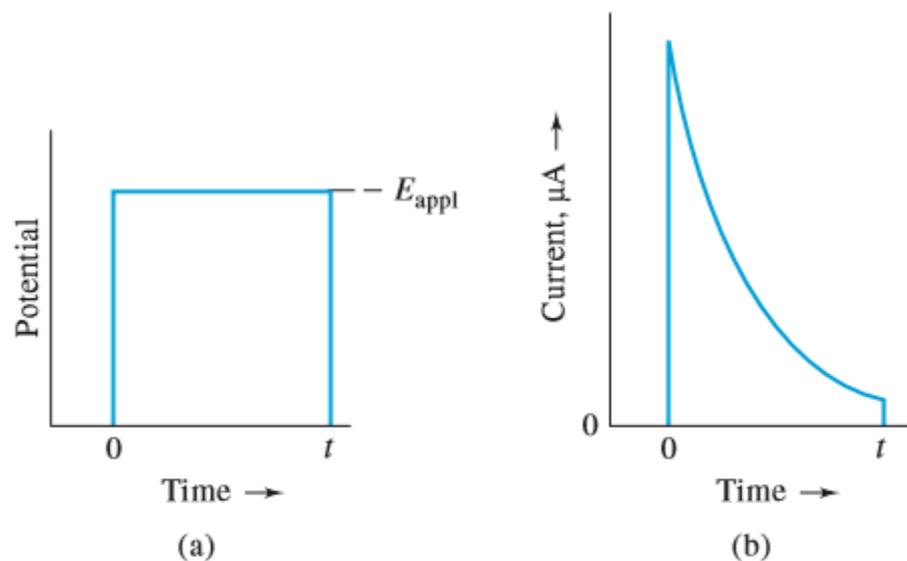
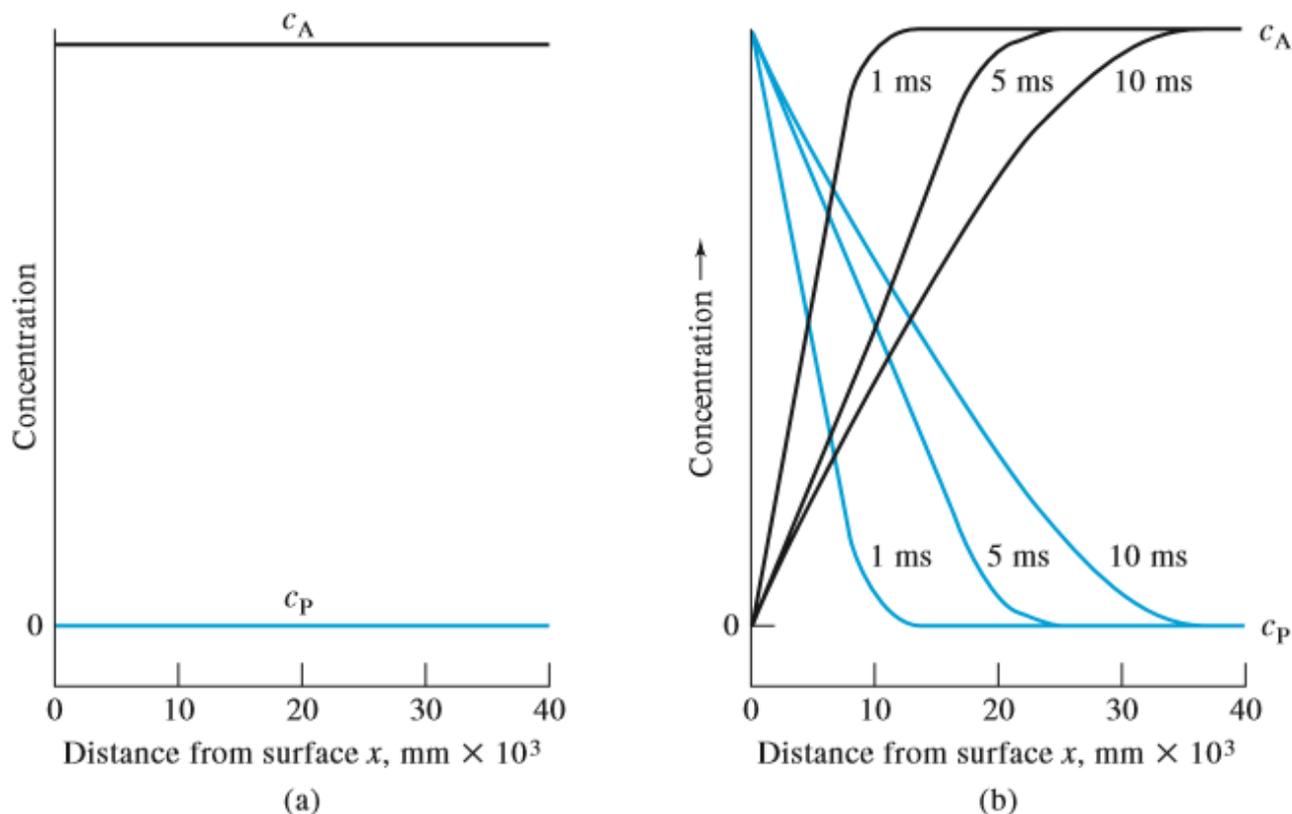


FIGURE 25-9 Current response to a potential step for a planar electrode in an unstirred solution. (a) Excitation profile. (b) Current response.

Initially, the current rises to a peak value that is required to convert essentially all of A in the surface layer of solution to P. Diffusion from the bulk of the solution then brings more A into this surface layer where further reduction occurs. The current required to keep the concentration of A at the level required by Equation 25-3 decreases rapidly with time, however, because A must travel greater and greater distances to reach the surface layer where it can be reduced. Thus, as seen in Figure 25-9b, the current drops off rapidly after its initial surge.

➤ Profiles for Planar Electrodes in Unstirred Solutionscont'd

- NO STIRRING (IN THE ABSENCE OF CONVECTION) - DIFFUSION CONTROLLED REDUCTION



The current i required to produce these gradients is proportional to the slopes of the straight-line portions of the solid lines in Figure 25-10b.

$$i = nFAD_A \left(\frac{\partial c_A}{\partial x} \right)$$

A : electrode surface area (cm^2),
 D_A : diffusion coeff. for A (cm^2/s),
 c_A : concentration of A (mol/cm^3)

FIGURE 25-10 Concentration distance profiles during the diffusion-controlled reduction of A to give P at a planar electrode. (a) $E_{\text{appl}} = 0 \text{ V}$. (b) $E_{\text{appl}} = \text{point Z in Figure 25-6}$; elapsed time: 1, 5, and 10 ms.

It is not practical to obtain limiting currents with planar electrodes in unstirred solutions because the currents continually decrease with time as the slopes of the concentration profiles become smaller.

The product $D_A \left(\frac{\partial c_A}{\partial x} \right)$ is called the flux, which is the number of moles of A per unit time per unit area diffusing to the electrode.

➤ Profiles for Planar Electrodes in Stirred Solutions

- Let us consider electrode immersed in a solution that is stirred vigorously.
- To understand the effect of stirring, we must develop a picture of liquid flow patterns in a stirred solution containing a small planar electrode. We can identify two types of flow depending on the average flow velocity .
 - *Laminar flow* occurs at low flow velocities and has smooth and regular motion as depicted on the left in the figure.
 - *Turbulent flow*, on the other hand, happens at high velocities and has irregular, fluctuating motion as shown on the right.
- we have a region of turbulent flow in the bulk of solution far from the electrode and a region of laminar flow close to the electrode.

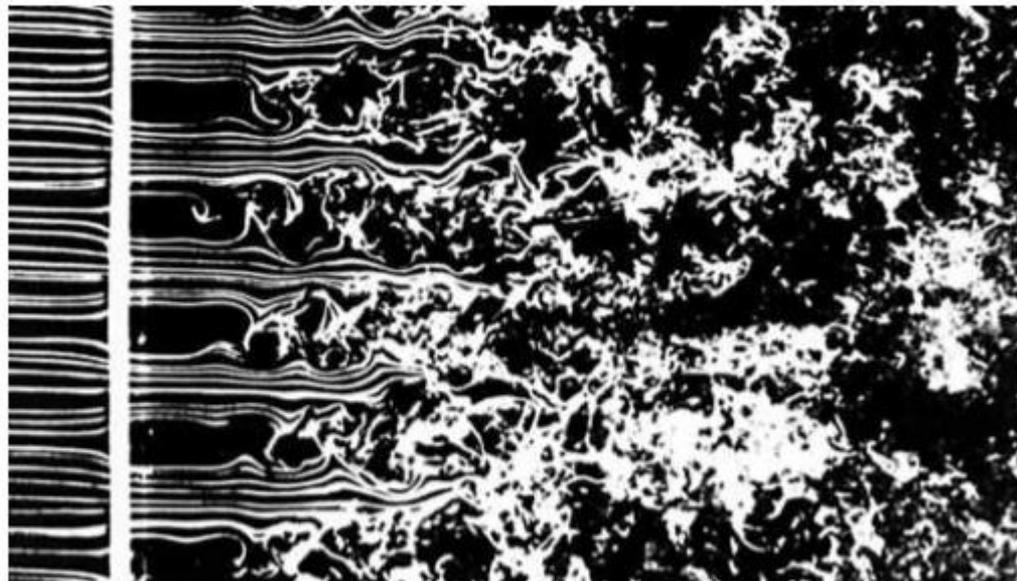


FIGURE 25-11 Visualization of flow patterns in a flowing stream. Turbulent flow, shown on the right, becomes laminar flow as the average velocity decreases to the left. In turbulent flow, the molecules move in an irregular, zigzag fashion and there are swirls and eddies in the movement. In laminar flow, the streamlines become steady as layers of liquid slide by each other in a regular manner.

- In the laminar-flow region, the layers of liquid slide by one another in a direction parallel to the electrode surface. Very near the electrode, at a distance d centimeters from the surface, frictional forces give rise to a region where the **flow velocity is zero**. The thin layer of solution in this region is a stagnant layer called the **Nernst diffusion layer**.

-in the Nernst diffusion layer:
the concentrations of reactant and product vary as a function of distance from the electrode surface and that there are concentration gradients.
-throughout the laminar-flow and turbulent-flow regions,
convection maintains the concentration of A at its original value and the concentration of P at a very low level.

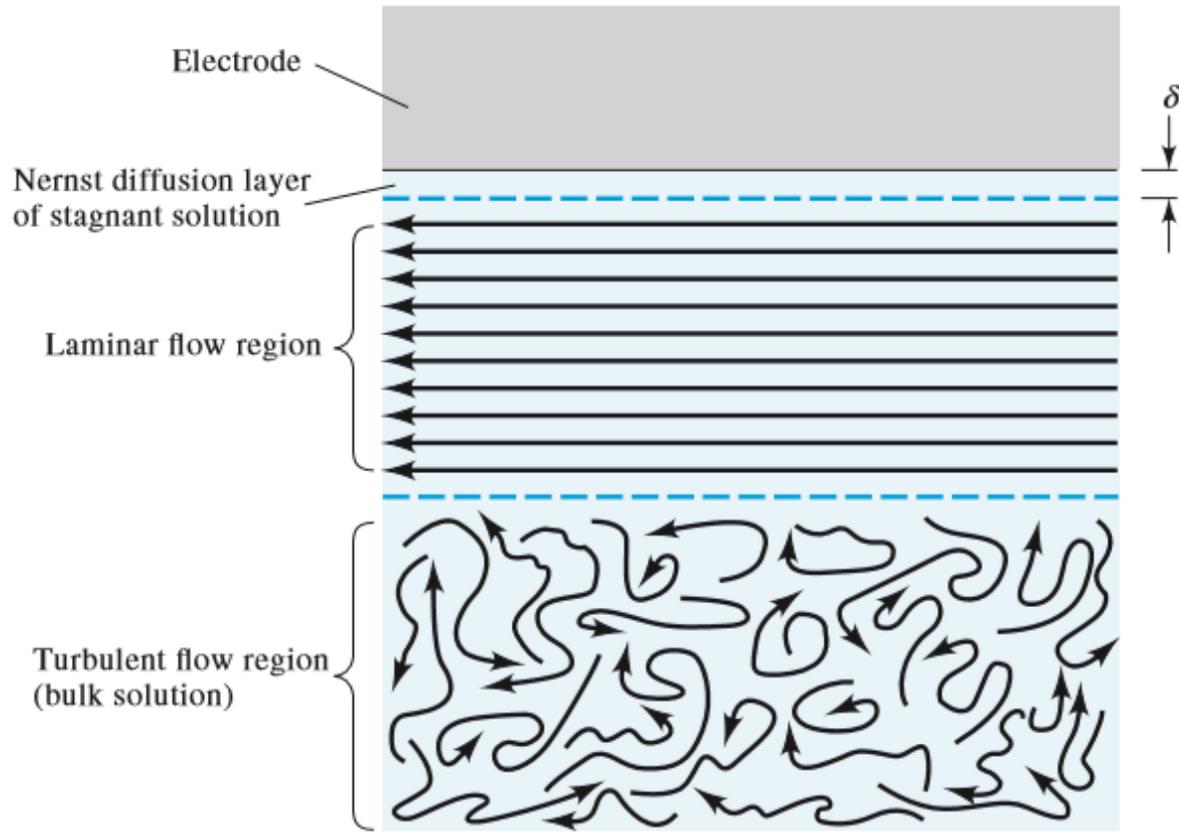
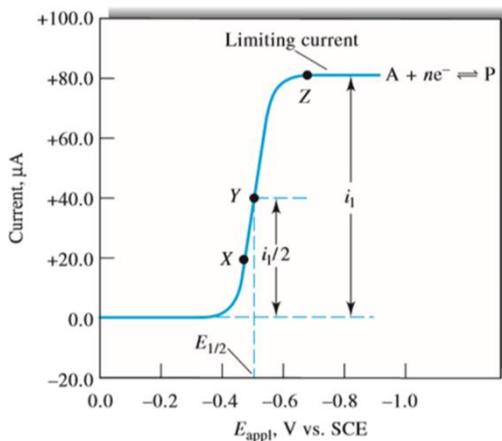


FIGURE 25-12 Flow patterns and regions of interest near the working electrode in hydrodynamic voltammetry.

Concentration profiles for A and P at potentials X, Y, and Z



the solution is divided into two regions.

1) The bulk of the solution (turbulent- and laminar-flow regions) is shown in Figure 25-12, where mass transport takes place by mechanical convection brought about by the stirrer. The concentration of A throughout this region is c_A , whereas c_P is essentially zero.

2) The second region is the Nernst diffusion layer, which is immediately adjacent to the electrode surface and has a thickness of δ centimeters. δ ranges from 10^{-2} to 10^{-3} cm, depending on the efficiency of the stirring and the viscosity of the liquid.

Within the static diffusion layer, mass transport takes place by diffusion alone, just as was the case with the unstirred solution. With the stirred solution, however, diffusion is limited to a narrow layer of liquid, which even with time cannot extend indefinitely into the solution. As a result, steady, diffusion-controlled currents appear shortly after applying a voltage.

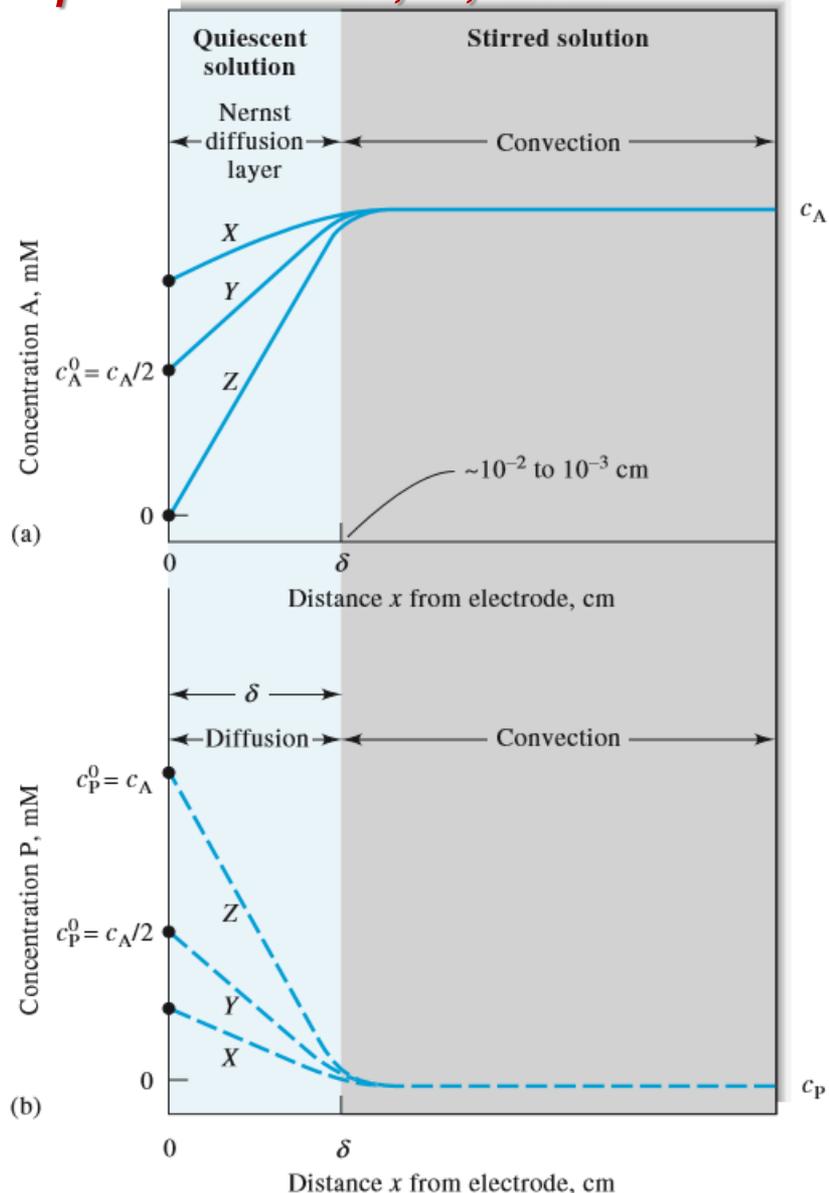


FIGURE 25-13 Concentration profiles at an electrode-solution interface during the electrolysis $A + ne^- \rightarrow P$ from a stirred solution of A. See Figure 25-6 for potentials corresponding to curves X, Y, and Z.

Concentration profiles for A and P at potentials X, Y, and Z

- at potential X, the equilibrium concentration of A at the electrode surface has been reduced to about 80% of its original value and the equilibrium concentration P has increased by an equivalent amount; that is, $c_P^0 = c_A - c_A^0$.
- At potential Y, which is the half-wave potential, the equilibrium concentrations of the two species at the surface are approximately the same and equal to $c_A/2$.
- Finally, at potential Z and beyond, the surface concentration of A approaches zero, and that of P approaches the original concentration of A, c_A . Thus, at potentials more negative than Z, essentially all A ions entering the surface layer are instantaneously reduced to P.

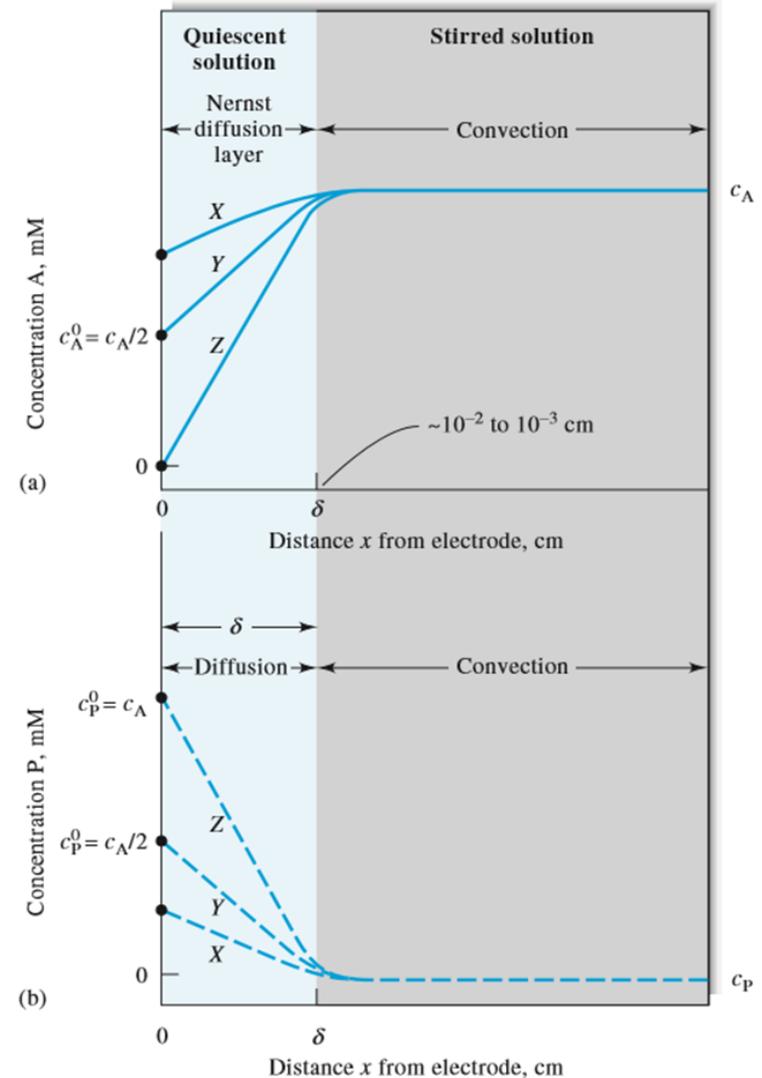


FIGURE 25-13 Concentration profiles at an electrode-solution interface during the electrolysis $A + ne^- \rightarrow P$ from a stirred solution of A. See Figure 25-6 for potentials corresponding to curves X, Y, and Z.

25C-2 Voltammetric currents

- ⇒ The current at any point in the electrolysis is determined by the rate of transport of A from the outer edge of the diffusion layer to the electrode surface.
- ⇒ Because the product of the electrolysis P diffuses from the surface and is ultimately swept away by convection, a continuous current is required to maintain the surface concentrations demanded by the Nernst equation.
- ⇒ Convection, however, maintains a constant supply of A at the outer edge of the diffusion layer. Thus, a steady-state current results that is determined by the applied potential. This current is a quantitative measure of how fast A is being brought to the surface of the electrode, and this rate is given by $\partial C_A / \partial x$ where x is the distance in centimeters from the electrode surface. For a planar electrode, the current given by Equation 25-4.

$$i = nFAD_A \left(\frac{\partial c_A}{\partial x} \right)$$

- ⇒ $\partial C_A / \partial x$ is the slope of the initial part of the concentration profiles shown in Figure 25-13a, and these slopes can be approximated by $(C_A - C_A^0) / \delta$. When this approximation is valid, Equation 25-4 reduces to

$$i = \frac{nFAD_A}{\delta} (c_A - c_A^0) = k_A (c_A - c_A^0)$$

where $k_A = nFAD_A / \delta$

- ⇒ as C_A^0 becomes smaller as a result of a larger negative applied potential, the current increases until the surface concentration approaches zero, at which point the current becomes constant and independent of the applied potential. Thus, when $C_A^0 \rightarrow 0$, the current becomes the limiting current i_l , and Equation 25-5 reduces to Equation 25-6.

$$i_l = \frac{nFAD_A}{\delta} c_A = k_A c_A$$

- ⇒ Nevertheless, this simplified model does provide a reasonable approximation of the relationship between the current and the variables that affect the current.

Current-Voltage Relationships for Reversible Reactions

⇒ To develop an equation for the sigmoid curve we substitute Equation 25-6 into Equation 25-5 and rearrange, which gives

$$c_A^0 = \frac{i_l - i}{k_A}$$

⇒ The surface concentration of P can also be expressed in terms of the current by using a relationship

$$i = -\frac{nFAD_P}{\delta}(c_P - c_P^0)$$

⇒ the concentration of P approaches zero in the bulk of the solution and, therefore, when $c_P \sim 0$

$$i = \frac{-nFAD_P c_P^0}{\delta} = k_P c_P^0$$

where $k_P = nFAD_P / \delta$. Rearranging gives

$$c_P^0 = i / k_P$$

⇒ After rearrangement

$$E_{\text{appl}} = E_A^0 - \frac{0.0592}{n} \log \frac{k_A}{k_P} - \frac{0.0592}{n} \log \frac{i}{i_l - i} - E_{\text{ref}} \quad (25-11)$$

⇒ When $i = i_l/2$, the third term on the right side of this equation becomes equal to zero, and, by definition, E_{appl} is the half-wave potential. That is,

$$E_{\text{appl}} = E_{1/2} = E_A^0 - \frac{0.0592}{n} \log \frac{k_A}{k_P} - E_{\text{ref}} \quad (25-12)$$

⇒ Substituting this expression into Equation 25-11 gives an expression for the voltammogram in Figure 25-6. That is,

$$E_{\text{appl}} = E_{1/2} - \frac{0.0592}{n} \log \frac{i}{i_l - i}$$

⇒ Often, the ratio k_A/k_P in Equation 25-11 and in Equation 25-12 is nearly unity, so that we may write for the species A

$$E_{1/2} \approx E_A^0 - E_{\text{ref}}$$

Current-Voltage Relationships for Irreversible rxn

- Many voltammetric electrode processes, particularly those associated with organic systems, are irreversible, which leads to drawn-out and less well-defined waves.
- To describe these waves quantitatively requires an additional term in Equation 25-12 involving the activation energy of the reaction to account for the kinetics of the electrode process.
- Although half-wave potentials for irreversible reactions ordinarily show some dependence on concentration, diffusion currents remain linearly related to concentration. Some irreversible processes can, therefore, be adapted to quantitative analysis if suitable calibration standards are available.

Voltammograms for Mixtures of Reactants

- The reactants of a mixture generally behave independently of one another at a working electrode. Thus, a voltammogram for a mixture is just the sum of the waves for the individual components.

- Figure 25-14 shows the voltammograms for a pair of two-component mixtures. The half-wave potentials of the two reactants differ by about 0.1 V in curve A and by about 0.2 V in curve B.

- Note that a single voltammogram may permit the quantitative determination of two or more species provided there is sufficient difference between succeeding half-wave potentials to permit evaluation of individual limiting currents. Generally, a difference of 0.1 to 0.2 V is required if the more easily reducible species undergoes a two-electron reduction; a minimum of about 0.3 V is needed if the first reduction is a one-electron process.

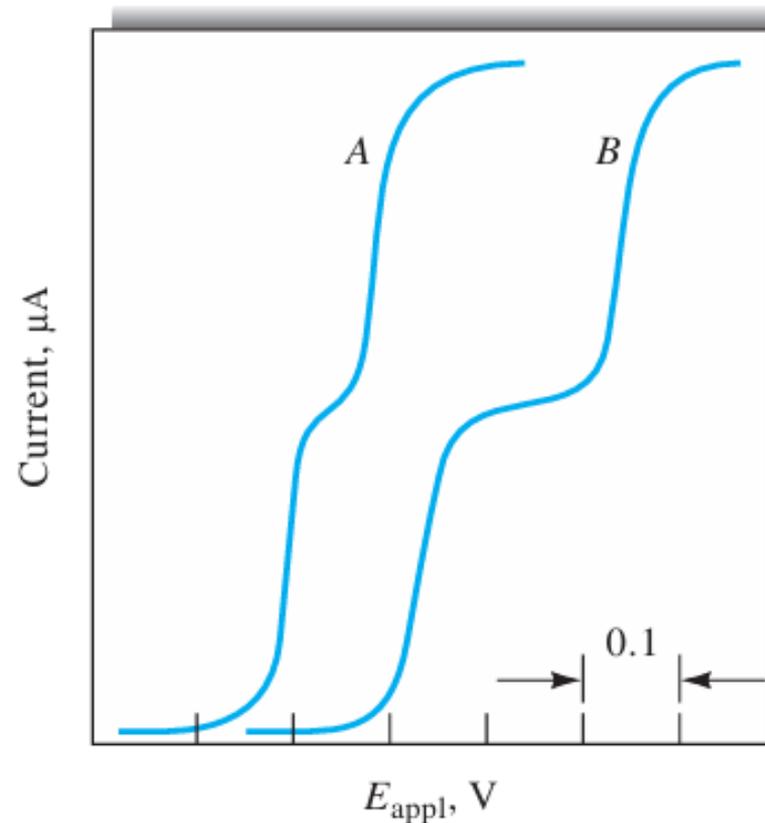


Figure 25-14 Voltammograms for two-component mixtures. Half-wave potentials differ by 0.1 V in curve A and by 0.2 V in curve B.

Anodic and Mixed Anodic-Cathodic Voltammograms

- **an anodic wave (curve A)**; the electrode reaction is the oxidation of iron(II) to iron(III) in the presence of citrate ion. A limiting current is observed at about + 0.1 V (versus the SCE), which is due to the half-reaction $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{e}^-$

• **Curve C** represents the voltammogram for a **cathodic wave**; Here, results from reduction of iron(III) to iron (II). The half-wave potential is identical with that for the anodic wave, indicating that the oxidation and reduction of the two iron species are perfectly reversible at the working electrode.

• **Curve B** is the voltammogram of an equimolar mixture of iron(II) and iron(III). The portion of the curve below the zero-current line corresponds to the oxidation of the iron(II); this reaction ceases at an applied potential equal to the half-wave potential. The upper portion of the curve is due to the reduction of iron(III).

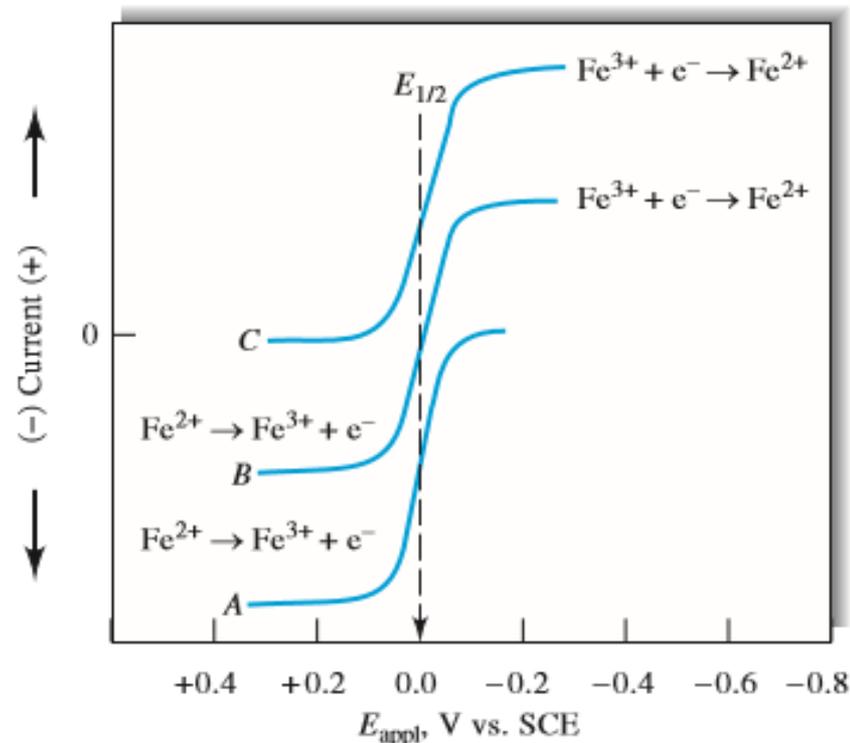


FIGURE 25-15 Voltammetric behavior of iron(II) and iron(III) in a citrate medium. Curve A: anodic wave for a solution in which $c_{\text{Fe}^{2+}} = 1 \times 10^{-4}$ M. Curve B: anodic-cathodic wave for a solution in which $c_{\text{Fe}^{2+}} = c_{\text{Fe}^{3+}} = 0.5 \times 10^{-4}$ M. Curve C: cathodic wave for a solution in which $c_{\text{Fe}^{3+}} = 1 \times 10^{-4}$ M.

25C-3 Oxygen waves

- Voltammetric measurements offer a convenient and widely used method for determining dissolved oxygen in solutions. However, the presence of oxygen often interferes with the accurate determination of other species
- Thus, oxygen removal is usually the first step in voltammetric and amperometric procedures.

➤ Oxygen can be removed by passing an inert gas through the analyte solution for several min.

(sparging)

➤ A stream of the same gas, usually nitrogen, is passed over the surface of the solution during analysis to prevent the reabsorption of oxygen.

• Dissolved oxygen is easily reduced at many working electrodes. An aqueous solution sat'd with air exhibits two distinct oxygen waves.

• The first results from the reduction of oxygen to H_2O_2

• The second wave corresponds to the further

reduction of the H_2O_2

• Because both reactions are two-electron reductions, the two waves are of equal height

• The lower curve in the Figure is a voltammogram of an oxygen-free solution.

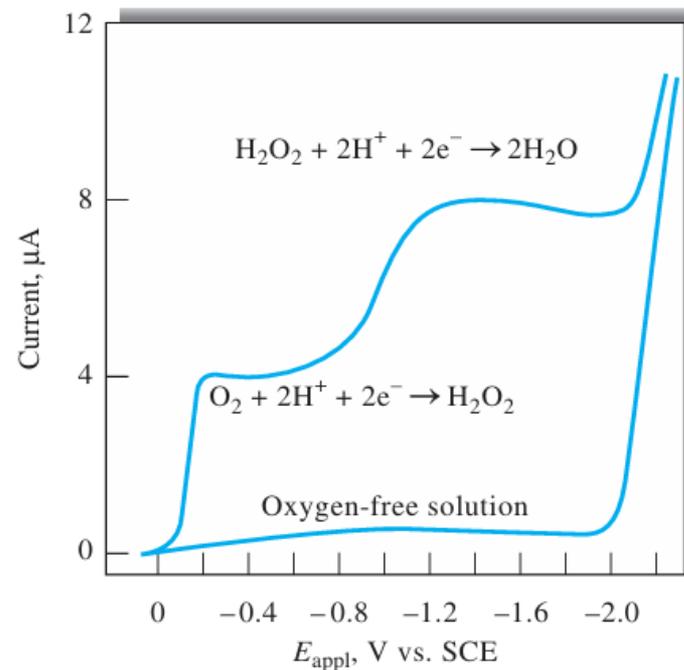


FIGURE 25-16 Voltammogram for the reduction of oxygen in an saturated 0.1-M KCl solution. The lower curve is for a 0.1-M solution in which the oxygen is removed by bubbling nitrogen through the solution.

25C-4 Applications of Hydrodynamic voltammetry

The most important uses of hydrodynamic voltammetry include

- (1) detection and determination of chemical species as they exit from chromatographic columns or flow-injection apparatus
- (2) routine determination of oxygen and certain species of biochemical interest, such as glucose, lactose, and sucrose;
- (3) detection of end points in coulometric and volumetric titrations; and
- (4) fundamental studies of electrochemical processes.

1) Voltammetric Detectors in Chromatography and FIA

- Hydrodynamic voltammetry is widely used for detection and determination of oxidizable or reducible compounds or ions that have been separated by liquid chromatography or that are produced by flow-injection methods.
- A thin-layer cell such as the one shown schematically in Figure 25-17a is used in these applications.
- The working electrode in these cells is usually embedded in the wall of an insulating block separated from a counter electrode by a thin spacer as shown. The volume of such a cell is typically 0.1 to 1 μL .
- A voltage corresponding to the limiting-current region for analytes is applied between the working electrode and a silver-silver chloride reference electrode that is located downstream from the detector.

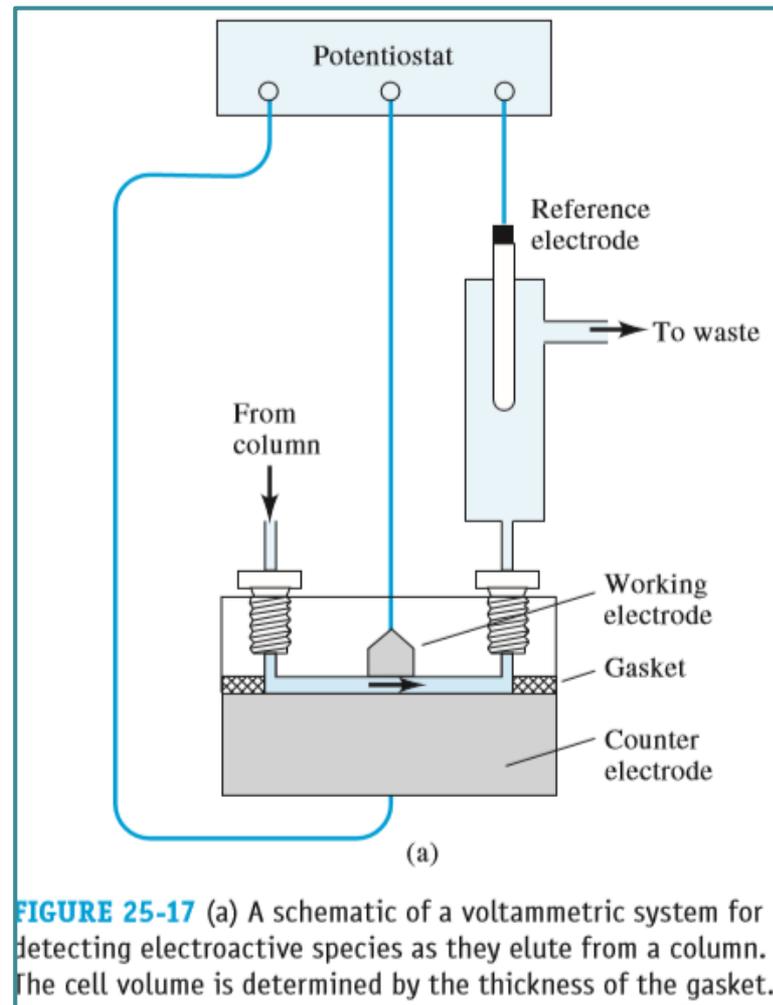


FIGURE 25-17 (a) A schematic of a voltammetric system for detecting electroactive species as they elute from a column. The cell volume is determined by the thickness of the gasket.

2) Voltammetric and Amperometric Sensors

- A number of voltammetric systems are available commercially for the determination of specific species in industrial, biomedical, environmental, and research applications.
- These devices are sometimes called electrodes or detectors but are, in fact, complete voltammetric cells and are better referred to as sensors.
- Two commercially available sensors, oxygen sensors, and enzyme sensors

Oxygen Sensors:

The determination of dissolved oxygen in a variety of aqueous environments, such as seawater, blood, sewage, effluents from chemical plants, and soils, is of tremendous importance to industry, biomedical and environmental research, and clinical medicine. One of the most common and convenient methods for making such measurements is with the Clark oxygen sensor, which was patented by L. C. Clark Jr. in 1956

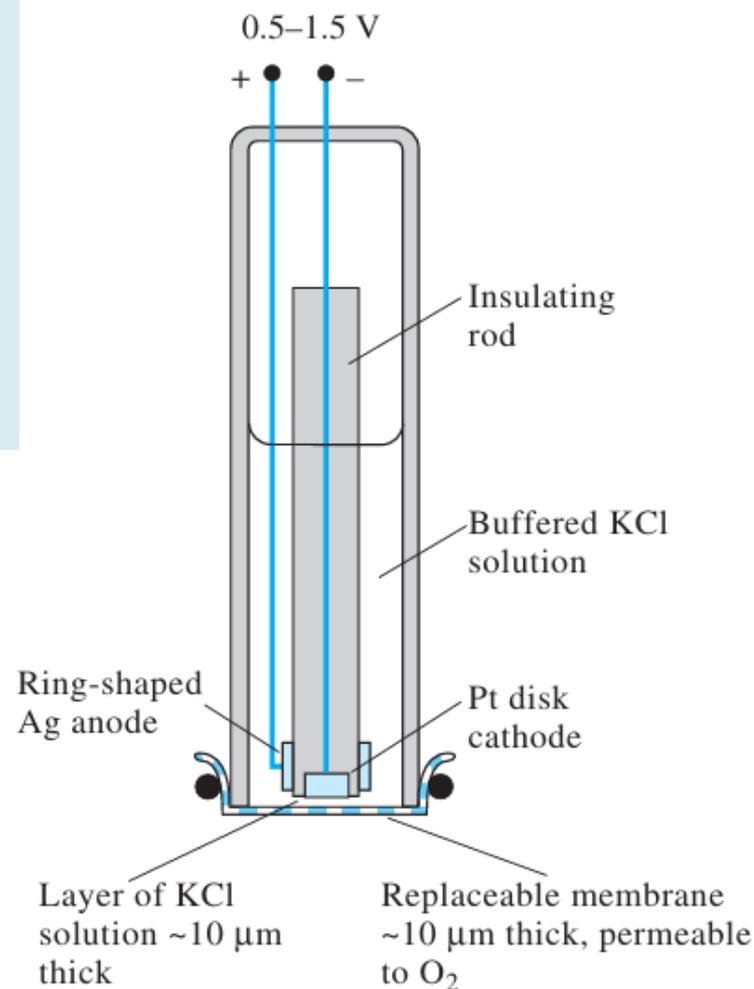


FIGURE 25-18 The Clark voltammetric oxygen sensor. Cathodic reaction: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$. Anodic reaction: $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl}(\text{s}) + \text{e}^-$.

Oxygen Sensors:

•When the oxygen sensor is immersed in a solution of the analyte, oxygen diffuses through the membrane into the thin layer of electrolyte immediately adjacent to the disk cathode, where it diffuses to the electrode and is immediately reduced to water. In contrast with a normal hydrodynamic electrode, two diffusion processes are involved—one through the membrane and the other through the solution between the membrane and the electrode surface. For a steady-state condition to be reached in a reasonable period (10 to 20 s), the thickness of the membrane and the electrolyte film must be 20 μm or less. Under these conditions, it is the rate of equilibration of the transfer of oxygen across the membrane that determines the steady-state current that is reached.

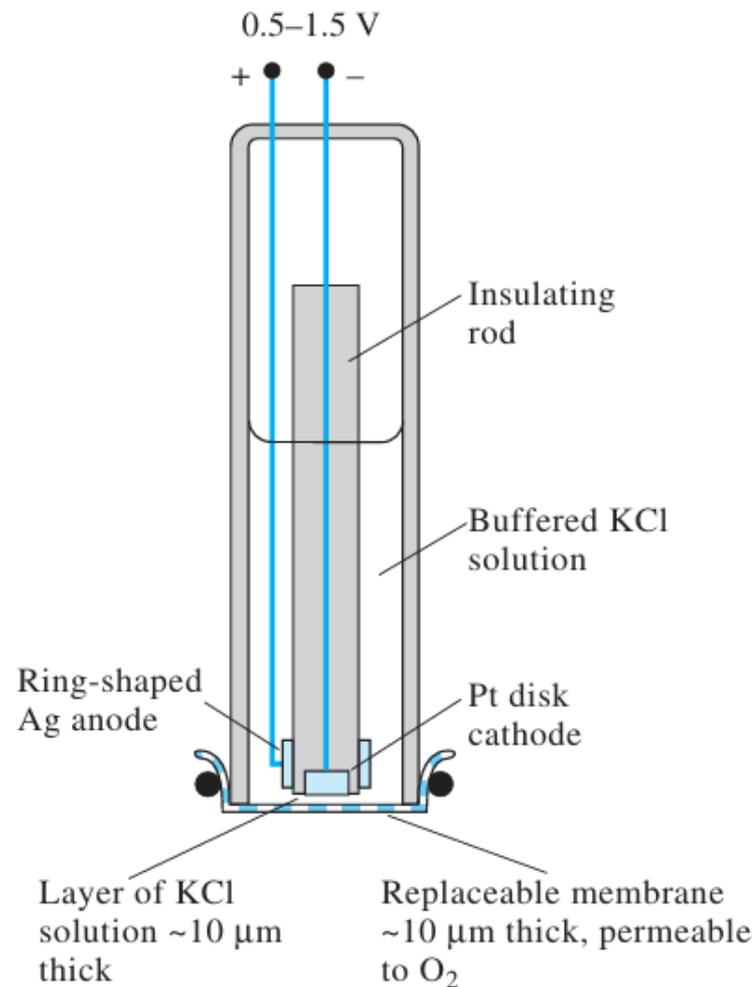
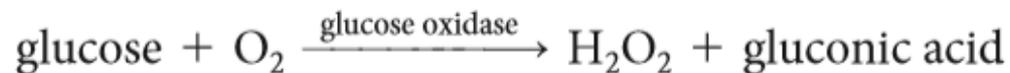


FIGURE 25-18 The Clark voltammetric oxygen sensor. Cathodic reaction: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$. Anodic reaction: $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl}(s) + \text{e}^-$.

Enzyme-Based Sensors, Glucose sensor :

- A number of enzyme-based voltammetric sensors are available commercially. An example is a glucose sensor that is widely used in clinical laboratories for the routine determination of glucose in blood serum.
- This device is similar in construction to the oxygen sensor shown in Figure 25-18.
- The membrane in this case is more complex and consists of three layers. The outer layer is a polycarbonate film that is permeable to glucose but impermeable to proteins and other constituents of blood.
- The middle layer is an immobilized enzyme (see Section 23F-2), glucose oxidase in this example. The inner layer is a cellulose acetate membrane, which is permeable to small molecules, such as hydrogen peroxide.
- When this device is immersed in a glucose-containing solution, glucose diffuses through the outer membrane into the immobilized enzyme, where the following catalytic reaction occurs:



- The hydrogen peroxide then diffuses through the inner layer of membrane and to the electrode surface, where it is oxidized to give oxygen. That is,

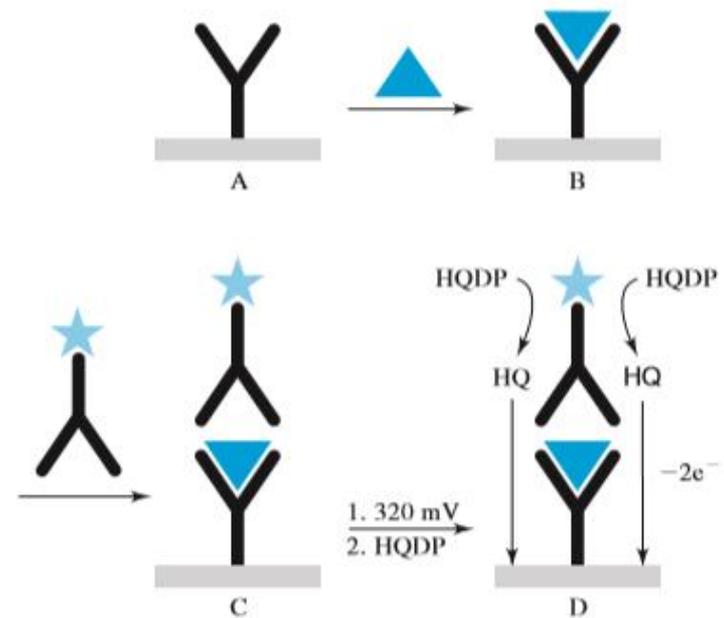


- The resulting current is directly proportional to the glucose concentration of the analyte solution. A variation on this type of sensor is often found in home glucose monitors widely used by diabetic patients. This device is one of the largest-selling chemical instruments in the world.

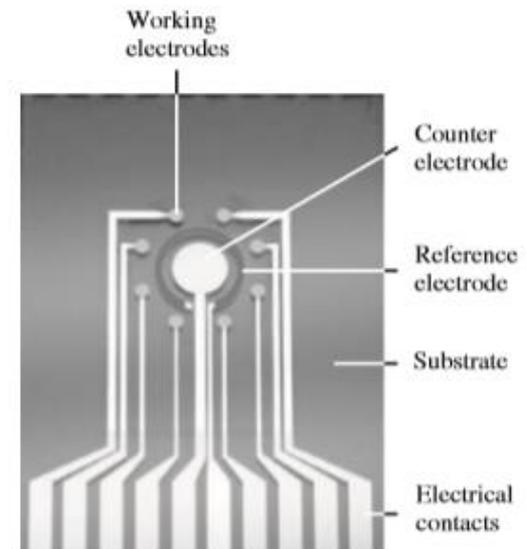
Immunosensors:

- Sensor specificity is often achieved by using molecular recognition elements that react exclusively with the analyte.
- Antibodies are proteins that have exceptional specificity toward analytes and are the recognition elements most commonly used in immunosensors.
- Immunosensors are typically fabricated by immobilizing antibodies on the sensor surface either through adsorption, covalent attachment, polymer entrapment, or other methods.

• (Figure 25-19a), an antibody appropriate for the desired analyte is immobilized by physical adsorption on the surface of an electrode (A). When the electrode is in contact with a solution containing the analyte, which is represented as blue triangles in the figure, it binds preferentially with the antibody (B). The electrode is then rinsed and brought into contact with a second antibody that has been tagged, or labeled, which is indicated by the stars in the figure (C). In this example, the antibody is tagged with the enzyme alkaline phosphatase, which catalyzes the conversion of hydroquinone diphosphate to hydroquinone. When a voltage of 320 mV versus Ag-AgCl is applied to the working electrode, hydroquinone undergoes a two-electron oxidation to quinone (D). The resulting current is directly proportional to the original concentration of the analyte.



(a)



(b)

- Electrochemical methods are used
 - To investigate electron transfer processes and kinetics
 - To study redox processes in organic and organometallic chemistry
 - To investigate multi-electron transfer processes in biochemistry and macromolecular chemistry
 - To determine adsorption processes on surfaces
 - To determine electron transfer and reaction mechanisms
 - To determine of thermodynamic properties of solvated species

- **Methods**

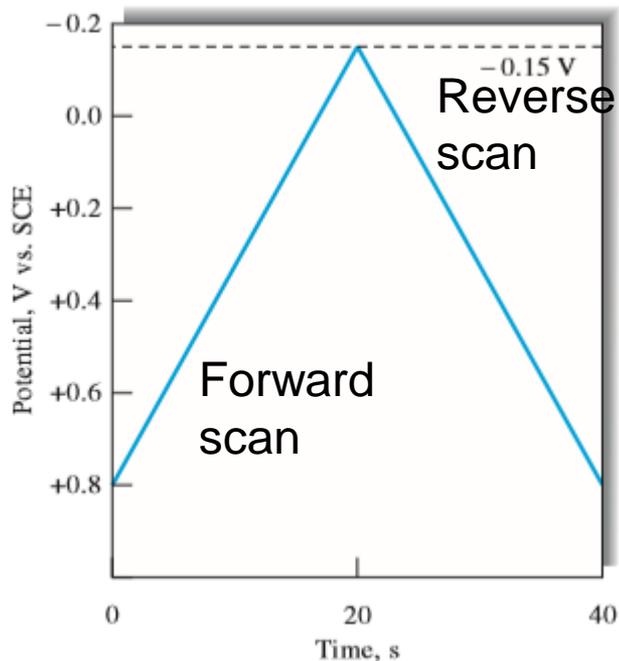
- *Polarography*: Often used mercury dropping electrodes because the drop is only used for one measurement and then discarded
- *Linear sweep voltammetry (LSV)*: the current at a working electrode is measured while the potential between the working electrode and a reference is swept linearly in time
- *Cyclic voltammetry*: the same as LSV but the potential is swept in a way that the experiment ends where it started

25D Cyclic Voltammetry

- ✓ Cyclic voltammetry is a very important electrochemical technique it can be used to study the redox behavior of compounds and to determine mechanisms and rates of oxidation/reduction reactions.
- ✓ Cyclic voltammetry is a simple extension of the linear sweep technique. Conventional cyclic voltammetry is especially informative about the qualitative aspects of an electrode process.
- ✓ The use of a triangular waveform at stationary electrodes, allows both the oxidation and reduction pathways to be studied conveniently from the experiment.
- ✓ Advise you to watch
 - ✓ <https://www.youtube.com/watch?v=cz67DnyS9-w>

25D Cyclic Voltammetry

- ✓ In cyclic voltammetry (CV), the current response of a small stationary electrode in an unstirred solution is excited by a triangular voltage waveform, such as that shown in Figure 25-23.
- ✓ In this example, the working electrode potential is first varied linearly from 0.8 V to -0.15 V versus an SCE. When the extreme of -0.15 V is reached, the scan direction is reversed, and the potential is returned to its original value of +0.8 V. The scan rate in either direction is 50 mV/s.
- ✓ This excitation cycle is often repeated several times. The voltage extrema at which reversal takes place (in this case, -0.15 and +0.8 V) are called *switching potentials*.



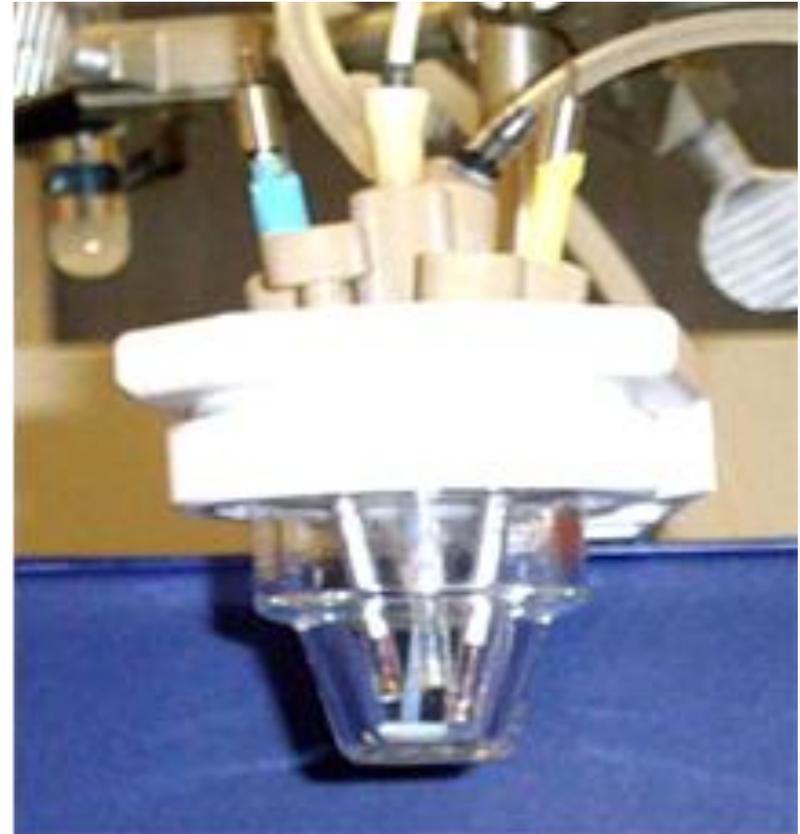
✓ The range of switching potentials chosen for a given experiment is one in which a diffusion-controlled oxidation or reduction of one or more analytes occurs.

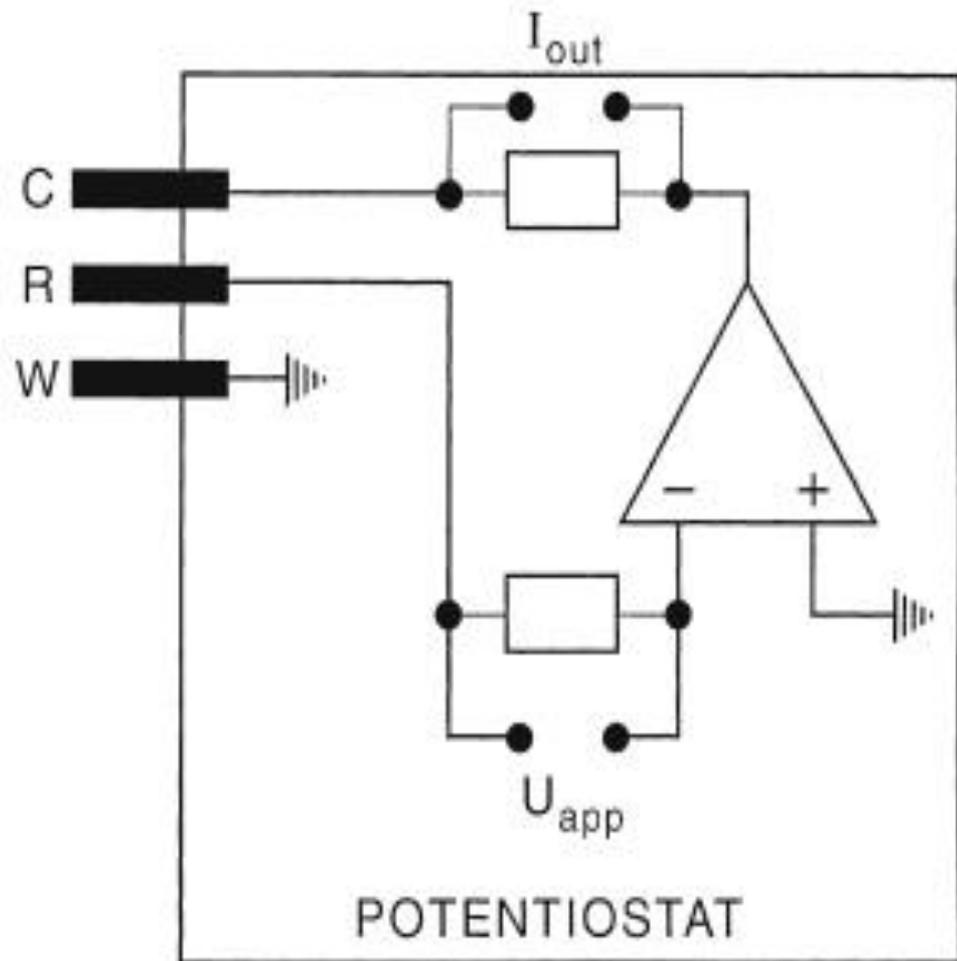
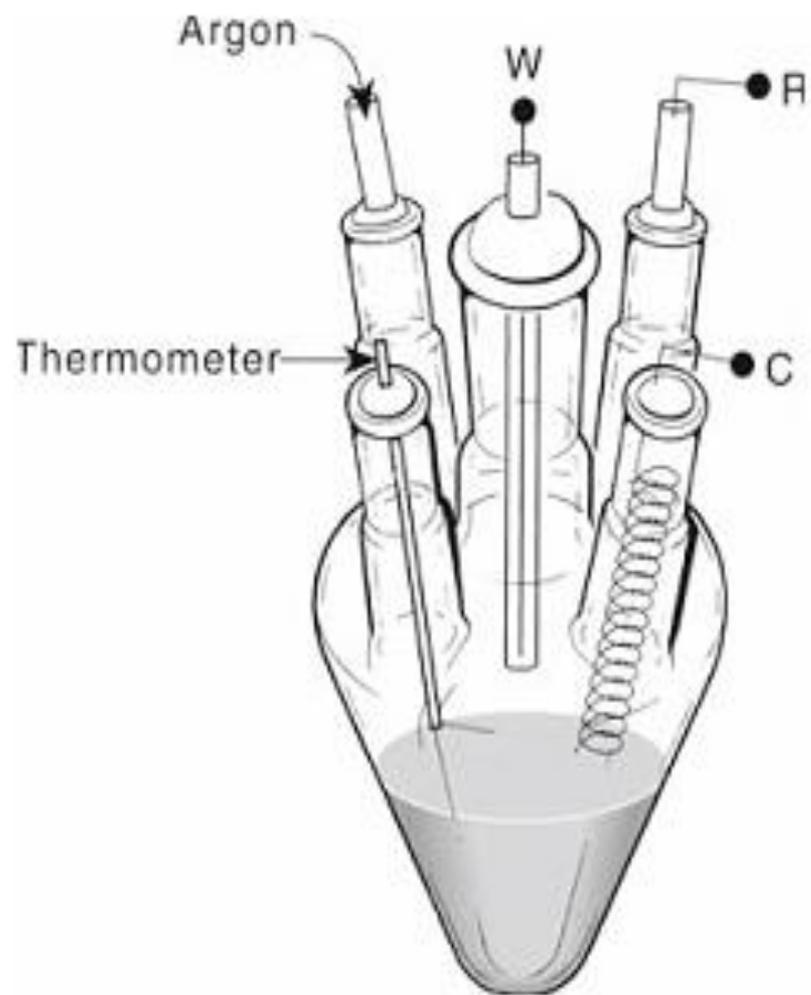
✓ The direction of the initial scan may be either negative, as shown, or positive, depending on the composition of the sample (a scan in the direction of more negative potentials is termed a **forward scan**, and one in the opposite direction is called a **reverse scan**). Generally, cycle times range from 1 ms or less to 100 s or more. In this example, the cycle time is 40 s.

FIGURE 25-23 Cyclic voltammetric excitation signal.

What is needed to run the experiment?

- Glass cell with the three electrodes
 - *Working electrode (left, glassy carbon in this course)
 - *Reference electrode (middle, Ag/AgCl/*0.1 M LiCl in dry acetone*)
 - *Auxiliary electrode (right, Pt-disk electrode)
- Three electrodes are needed because the measurement of the potential and the current have to be performed in different cycles because they interfere with each other.
- A gas line for ebulliating the solution with nitrogen is also evident on the upper right hand
- A potentiostat that allows for the control of the potential and the measurement of a current
- Computer system for control and recording





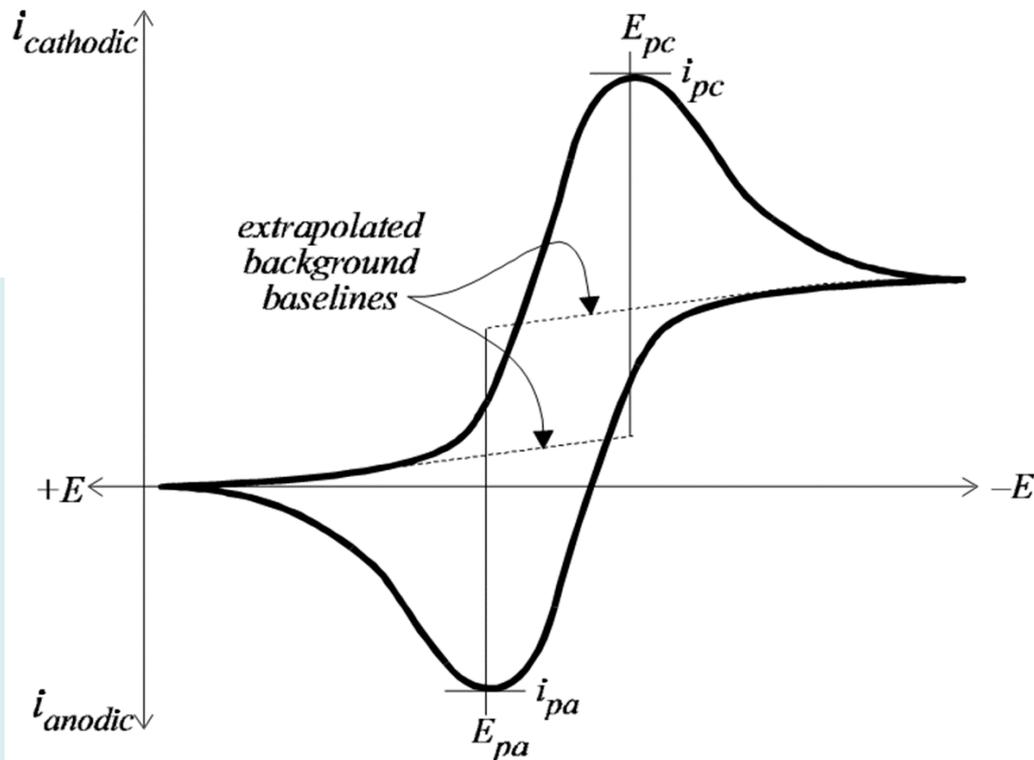
• Important variables in a cyclic voltammogram are

- The cathodic peak potential E_{pc} ,
- the anodic peak potential E_{pa} ,
- the cathodic peak current i_{pc} ,
- the anodic peak current i_{pa} .

- The potential is graphed along the x-axis with more positive (or oxidizing) potentials plotted to the left, and more negative (or reducing) potentials to the right.

-The current is plotted on the y-axis of the voltammogram, with cathodic (i.e., reducing) currents plotted up along the positive direction, and anodic (i.e., oxidizing) currents plotted down in the negative direction.

-A voltammogram is almost always plotted in this fashion by North American electrochemists, but in Europe, the axes are typically reversed.



- **Data analysis**

- The formal reduction potential is obtained by

- $E^0 = (E_{pa} + E_{pc})/2$

- The half peak potential $E_{1/2}$ can be described by the Nernst Equation

-

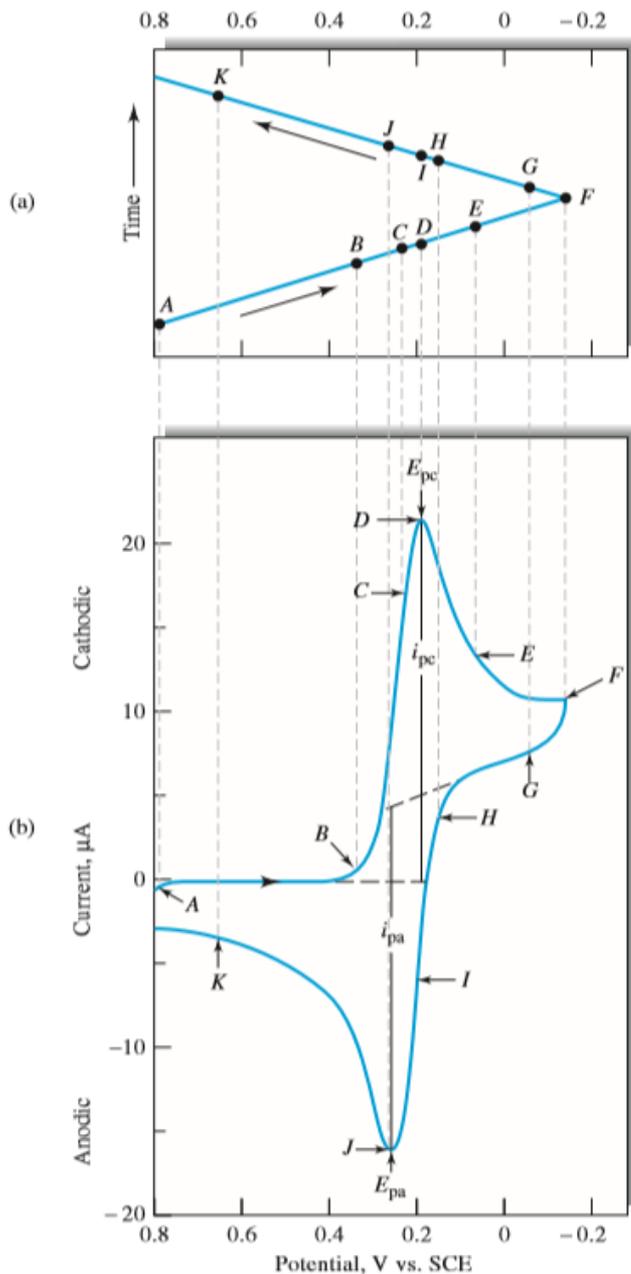
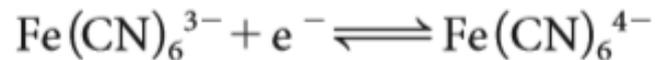


FIGURE 25-24 (a) Potential versus time waveform and (b) cyclic voltammogram for a solution that is 6.0 mM in $\text{K}_3\text{Fe}(\text{CN})_6$ and 1.0 M in KNO_3 . (From P. T. Kissinger and W. H. Heineman, *J. Chem. Educ.*, 1956, 33, 222.)

- The working electrode was a carefully polished stationary platinum electrode and the ref. elect. SCE.

- At the initial potential of +0.8 V, a tiny anodic current is observed, which immediately decreases to zero as the scan is continued. This initial negative current arises from the oxidation of water to give oxygen (at more positive potentials, this current rapidly increases and becomes quite large at about +0.9 V). No current is observed between a potential of +0.7 and +0.4 V because no reducible or oxidizable species is present in this potential range. When the potential becomes less positive than approximately +0.4 V, a cathodic current begins to develop (point B) because of the reduction of the hexacyanoferrate(III) ion to hexacyanoferrate(II) ion. The reaction at the cathode is then



- A rapid increase in the current occurs in the region of B to D as the surface concentration of Fe^{+3} smaller. The current at the peak is made up of two components.

- Cyclic voltammetry experiments are conducted *in unstirred solutions* using large (millimetric dimension) electrodes such that diffusion normal to the electrode is the major form of mass transport.
- The observed faradaic current depends on the kinetics and transport by diffusion of the electroactive species.
- The system is described as “reversible” when the electrode kinetics are much faster than the rate of diffusion. Anodic and cathodic peak currents are approximately equal in absolute value but opposite in sign. $i_{pa}/i_{pc} = 1$

The Nernst equation is obeyed for a reversible system. The difference in peak potentials, ΔE_p , is expected to be

$$\Delta E_p = |E_{pa} - E_{pc}| = 0.0592/n$$

- Quantitative information is obtained from the *Randles-Sevcik* equation, which at

$$i_p = 2.686 \times 10^5 n^{3/2} A c D^{1/2} v^{1/2}$$

where i_p is the peak current (A), A is the electrode area (cm²),
 D is the diffusion coefficient (cm²/s),
 c is the concentration (mol/cm³),
 and v is the scan rate (V/s).

For a reversible reaction, the peak current for the forward sweep of the first cycle is proportional to the concentration of the analyte and the square root of the sweep rate

CV offers a way of determining diffusion coefficients if the concentration, electrode area, and scan rate are known

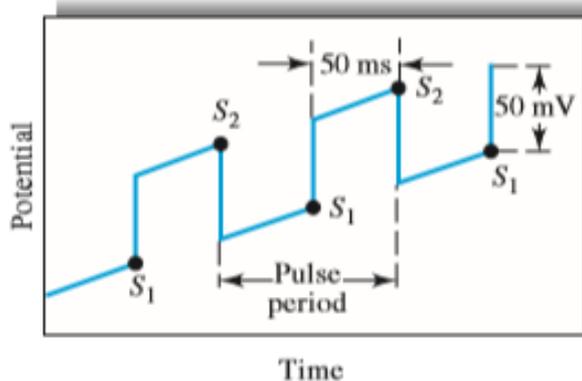
25E Pulse Voltammetry

- Many of the limitations of traditional linear-scan voltammetry were overcome by the development of pulse methods.
- The two most important pulse techniques,
 - differential-pulse voltammetry and
 - square-wave voltammetry.
- These methods are used with many different types of solid electrodes, the HMDE, and rotating electrodes

25E-1 Differential-Pulse Voltammetry

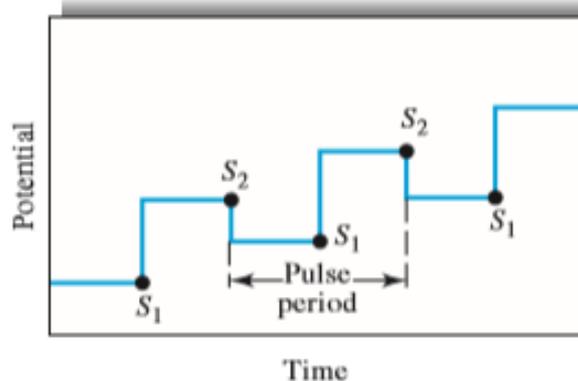
Small voltage pulses are superimposed on the linear voltage ramp, as in the figure below. The height of the pulse is called its modulation amplitude.

Pulse on linear scan



(a)

Pulse on staircase scan



(b)

Higher sensitivity;
Generally, detection limits with differential-pulse voltammetry are two to three orders of magnitude lower than those for classical voltammetry and lie in the range of 10^{-7} to 10^{-8} M.

FIGURE 25-29 Excitation signals for differential-pulse voltammetry.

25E-2 Square-wave voltammetry

- Square-wave voltammetry is a type of pulse voltammetry that offers the advantage of great speed and high sensitivity. An entire voltammogram is obtained in less than 10 ms.
- Square-wave voltammetry has been used with Hanging Mercury Dropping Electrodes, HMDEs and with other electrodes
- Square-wave voltammetry is a **large-amplitude differential technique** in which a waveform composed of a symmetric square wave, superimposed on a base staircase potential, is applied to the working electrode.
- The current is sampled twice during each square-wave cycle, *once at the end of the forward pulse (at t_1) and once at the end of the reverse pulse (at t_2)*.

Since the square-wave modulation amplitude is very large, the reverse pulses cause the reverse reaction of the product (of the forward pulse). The current difference between the two measurements is plotted versus the base staircase potential.

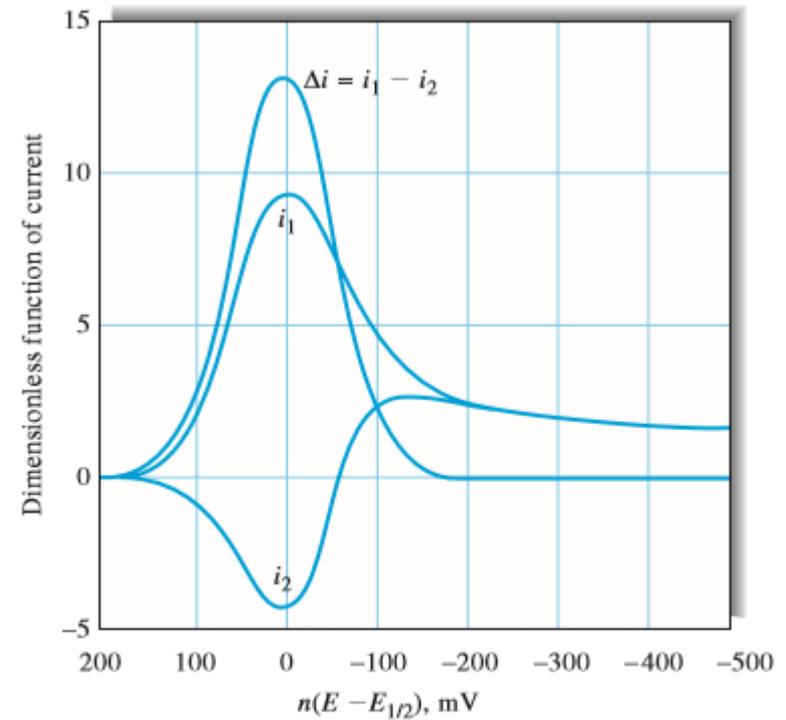


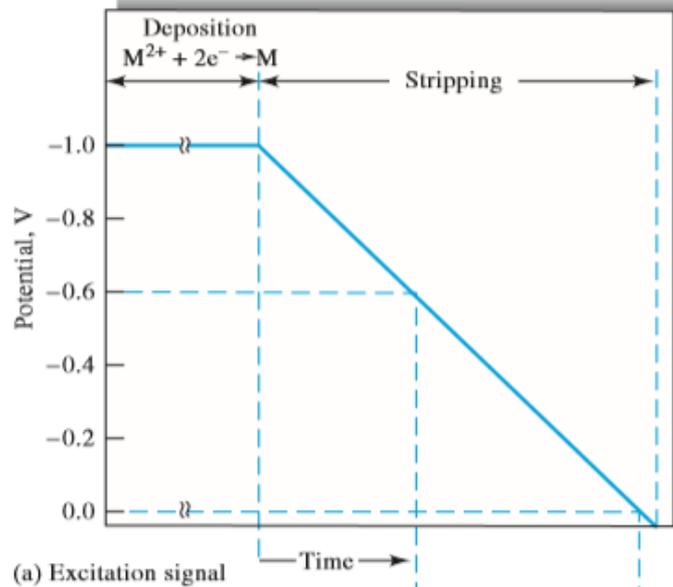
FIGURE 25-32 Current response for a reversible reaction to excitation signal in Figure 25-31c. This theoretical response plots a dimensionless function of current versus a function of potential, $n(E - E_{1/2})$ in millivolts. Here, i_1 = forward current; i_2 = reverse current; $i_1 - i_2$ = current difference. (From J. J. O'Dea,

25G APPLICATIONS OF VOLTAMMETRY

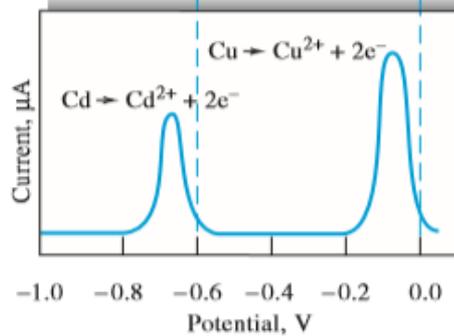
- In the past, linear-sweep voltammetry was used for the quantitative determination of a wide variety of inorganic and organic species, including molecules of biological and biochemical interest.
- Pulse methods have largely replaced classical voltammetry because of their greater sensitivity, convenience, and selectivity.
- Generally, quantitative applications are based on calibration curves in which peak heights are plotted as a function of analyte concentration.
- In some instances the standard-addition method is used in lieu of calibration curves. In either case, it is essential that the composition of standards resemble as closely as possible the composition of the sample, both as to electrolyte concentrations and pH. When this is done, relative precisions and accuracies in the range of 1% to 3% can often be achieved.
- Voltammetry is applicable to the analysis of many inorganic substances. Most metallic cations, for example, are reduced at common working electrodes.
- Several organic functional groups are reduced at common working electrodes, thus making possible the determination of a wide variety of organic compounds. Oxidizable organic functional groups can be studied voltammetrically with platinum, gold, carbon, or various modified electrodes.

25H STRIPPING METHODS

- Stripping methods encompass a variety of electrochemical procedures having a common, characteristic initial step.
- In all of these procedures, the analyte is first deposited on a working electrode, usually from a stirred solution. After an accurately measured period, the electrolysis is discontinued, the stirring is stopped, and the deposited analyte is determined by one of the voltammetric procedures described
- During this second step in the analysis, the analyte is redissolved or stripped from the working electrode; hence the name attached to these methods.
- In anodic stripping methods, the working electrode behaves as a cathode during the deposition step and as an anode during the stripping step, with the analyte being oxidized back to its original form.
- In a cathodic stripping method, the working electrode behaves as an anode during the deposition step and as a cathode during stripping. The deposition step amounts to an electrochemical preconcentration of the analyte; that is, the concentration of the analyte in the surface of the working electrode is far greater than it is in the bulk solution.
- As a result of the preconcentration step, stripping methods yield the lowest detection limits of all voltammetric procedures. For example, anodic stripping with pulse voltammetry can reach nanomolar detection limits for environmentally important species, such as Pb^{2+} , Cd^{2+} , Cu^{2+} , and Tl^{+} .



(a) Excitation signal



(b) Voltammogram

FIGURE 25-34 (a) Excitation signal for stripping determination of Cd^{2+} and Cu^{2+} . (b) Stripping voltammogram.

-Initially, a constant cathodic potential (-1 V) is applied to the working electrode, both cadmium and copper ions to be reduced and deposited as metals.

-The electrode is maintained at this potential for several minutes until a significant amount of the two metals has accumulated at the electrode.

-The stirring is then stopped for 30 s or so while the electrode is maintained at -1 V.

-The potential of the electrode is then decreased linearly to less negative values and the current in the cell is recorded as a function of time, or potential.

-Figure 25-34b resulting voltammogram. At a potential somewhat more negative than -0.6 V, cadmium starts to be oxidized, causing a sharp increase in the current. As the deposited cadmium is consumed, the current peaks and then decreases to its original level. A second peak for oxidation of the copper is then observed when the potential has decreased to approximately -0.1 V.

- The heights of the two peaks are proportional to the mass of deposited metal.
- Stripping methods / trace analysis/ preconcentration/ 10^{-6} to 10^{-9} M feasible / both simple and rapid.