

Electroanalytical Chemistry

Electrochemical Cell

All electrochemical measurements take place in an electrochemical cell. The cell consists of two electrodes immersed in electrically conductive solution. The electrodes are connected by a wire, generally through some measuring device. The cell is designed so that electrons are transferred through the wire from electrode to electrode rather than through solution.

In galvanic (also called voltaic or spontaneous) cells, the solutions associated with each electrode cannot mix or electrons will be transferred directly rather than through the electrodes. However, a solution connection must be maintained so that an excess of charge does not build up at the electrodes. This solution contact is usually called a "salt bridge." The term derived from tubes filled with a salt solution connected to both electrode solutions. A porous plug or agar gel prevents substantial mixing between the internal solution and the analytical solutions. True salt bridges (such as the one described) have been shown to be the most effective type of solution connection. However, the term has come to refer to any mechanism which allows a solution connection with negligible mixing.

Solutions. Solutions are normally made electrically conductive by addition of an *electrolyte* which produces high concentrations of ions in solution but does not affect the measurement. Typical electrolyte concentrations are about 0.1 M. Pure water is not sufficiently conductive and analytes, if ionic, are generally in concentrations too small to be effective.

The concentration of electrolyte is usually 10-100 times greater than that of analyte. It is, therefore, important to choose an electrolyte which will not interfere with the measurement. If the electrolyte produces even a small signal, this signal will be measured instead of that of the

analyte.

However, this high concentration does have a hidden advantage. Since most electrochemical measurements are dependent on activity rather than concentration, the high electrolyte concentration keeps the ionic strength, and therefore the activity coefficient, constant with variations in analyte concentration. At these high ionic strengths, although the activity coefficient will be far from unity and unmeasurable, it will be constant and this constant value of activity coefficient will be subsumed into a proportionality constant.

Electrodes. An electrochemical cell must consist of two electrodes with a half-reaction taking place at each electrode. The oxidation half-reaction occurs at the anode. The reduction half reaction takes place at the cathode. In electroanalytical chemistry, an electrode often alternates between being the anode and being the cathode. Consequently, the terms “anode” and “cathode” are rarely useful designations. Instead there is one electrode where reactions of interest occur, which is known as the *indicator electrode* in potentiometry and the *working electrode* in voltammetry, and at least one more electrode, used for comparison, which is called the reference electrode.

Since it is used for comparison, the *reference electrode* (which is really a half-cell) must be a system which has been very well characterized. Ideally, its potential should be known and constant. This can be problematic since electrochemical potential is dependent on concentration and temperature. (Experimental note: Since the reference electrode is really a half-cell, it must be connected to the solution by a salt bridge. Failure of the salt bridge of the reference electrode to be in contact with the solution is a common reason for inaccurate and imprecise measurements.)

Since it is impossible to measure the potential of a single electrode, a particular electrode

(half-cell) was arbitrarily assigned a value of zero. This electrode is the *standard hydrogen electrode* (SHE) which is also called the *normal hydrogen electrode* (NHE). It consists of a special platinum electrode called “platinum black” in which platinum foil is coated with a finely divided layer of platinum, hydrogen gas at one atmosphere pressure and hydrogen ion at an activity of one. This electrode is defined to have a potential of exactly zero volts at all temperatures. This half-reaction was chosen since most scientists are familiar with the reaction of hydrogen ion becoming hydrogen gas.

While this electrode makes good chemical and theoretical sense, it is obviously not practical to achieve and maintain the appropriate concentrations of hydrogen ion and gas. Instead, two other electrodes are commonly used as reference electrodes. These are the silver/silver chloride electrode (Ag/AgCl) and the saturated calomel electrode (SCE). Both of these electrodes make substantial use of solids and saturated solutions. This results in electrodes which are easy to make and activities which remain constant even if the half-cell undergoes some reaction.

The *silver/silver chloride electrode* consists of silver chloride coated on a silver wire and submerged in a saturated solution of potassium chloride which is connected to the solution of interest by a salt bridge. The potential of this electrode is 0.197 V more positive than an SHE. The potential is stable to 60°C. These electrodes are commercially available. Sometimes a 1.0 M aqueous solution of KCl is used instead of a saturated solution. The potential for a Ag/AgCl electrode with 1.0 M KCl is +0.222 V vs. SHE.

The *saturated calomel electrode* consists of liquid mercury in a saturated solution of mercury(I) chloride (calomel) and potassium chloride connected to the solution of interest by a

salt bridge. Although it is useful at in a smaller temperature range than the Ag/AgCl electrode, this electrode has been widely used because it is extremely easy to prepare. It is also commercially available. However, this electrode is losing popularity due to the toxicity concerns about mercury.

Electrochemical Measurements

Any process measured in electroanalytical chemistry occurs at the surface of the electrode. Therefore electrochemical measurements reflect an inherently surface process rather than a solution process. Hence, the surface itself, the distance of the analyte from the surface, the rate at which the analyte reaches the surface and interactions of analyte with the surface will all affect the measurement. The type and magnitude of the effect depends on the type of measurement. The measurement types are detailed below.

Potential (E). One of the more common electrochemical measurements is that of potential (E). Potential is more accurately called a “potential difference” since it always reflects the force at which the electrons move between electrodes. However, since it is impossible to measure the potential at one electrode, the two terms are used interchangeably.

Potential is related to the free energy (ΔG) of the overall reaction. Potential is determined by the specific reaction, concentration (more accurately, activity) of products and reactants and temperature according to the Nernst equation.

$$E = E^\circ + \frac{RT}{nF} \ln\left(\frac{[\text{ox}]}{[\text{red}]}\right) \quad (1)$$

where E is the experimental potential (V), E° is the standard potential (V) which is dependent on the identity of the reaction, R is the gas constant (J/mol·K), T is temperature (K), n is the number

of electrons transferred (mol e/mol), F is Faraday's constant (C/mol e), $[ox]$ is the activity of the oxidized form of the analyte and $[red]$ is the activity of the reduced form of the analyte. If other species, such as H^+ participate in the reaction their activities must be also be included.

Since the reaction of interest normally occurs at only one electrode, an electrode potential is measured. The term "electrode potential" superficially refers to the potential at one electrode.

Since this is an experimental impossibility, what it really refers to is the potential versus some known half-cell, such as one of the reference electrodes mentioned above. Therefore, when referring to a electrode potential *the reference electrode must always be cited*. For example, the potential of a copper electrode in a solution with $[Cu^{2+}] = 1.0\text{ M}$ is about $+0.3\text{ V vs. SHE}$.

Most tables of electrode potentials use SHE (NHE) as the reference electrode. Experimental data is more likely to use Ag/AgCl or SCE as the reference electrode. Conversions between reference electrodes are easily accomplished by using the value of the experimental reference electrode versus SHE. For example, since the SCE electrode is $+0.241\text{ V vs. SHE}$, to convert the potential versus SHE (E_{SHE}) from the potential versus SCE (E_{SCE}), you could use the equation

$$0.241 - E_{SCE} = E_{SHE} \quad (2)$$

One of the features of many electroanalytical measurements is the ability to control potential. Changing the potential can force nonspontaneous reactions to occur and increase the rate of reaction. By definition, a more positive potential induces and/or speeds up oxidation reactions while a more negative potential induces and/or speeds up reduction reactions.

Charge (Q). Charge is a measurement of the number of electrons. Faraday's constant relates coulombs (C), the electrical measurement of charge, to the number of electrons where

$$96,484 \text{ C} = 1 \text{ mole of electrons} \quad (3)$$

The half reaction can then be used to relate the moles of electrons to moles of analyte.

Current (i). The current is the rate at which electrons travel. It is expressed in amperes or amps (A) which is the same as coulombs per second. Consequently, an measurement of current is proportional to the *instantaneous* rate of the reaction.

There are many factors which influence the rate of reaction. These include: electrode surface area, reactant concentration, temperature, viscosity of solution, and applied potential. To use current as a signal to measure reactant concentration, the other factors must be kept constant.

In addition to the current from the chemical reaction, there is also a *background current*. This current can be due to electrolysis of impurities, electrolysis of solvent, electrolysis of the electrode surface material, and capacitive currents. Electrolysis of the solvent and electrode can be minimized or eliminated by working in only at potentials where these reactions do not occur at any significant rate. This range of potentials is called the *potential window*. Potential windows for typical solvent/electrode systems are shown in Figure 1. Capacitive current is caused by the electrode-solution interface behaving like an electrical capacitor, storing charge. As the potential difference increases, more charge is stored at the electrode. Therefore capacitive current can also be called charging current. Generally background current can be determined by measuring a blank and subtracting its current from the analyte signal.

Techniques

Potentiometry. Potentiometry is the measurement of the potential between an electrode which responds to the analyte (called an ion selective or indicator electrode) and a reference electrode in an electrically conductive solution. Because the reference electrode has, by design, a constant potential, the measured potential depends on the activity of analyte. The measurement is taken when there is no current flow.

The potential depends on the *activity* of the analyte, however *concentration* of analyte is normally the question of interest. In solutions with low (near zero) ionic strength, the activity coefficient approaches unity and concentration is equivalent to activity. However, it is not possible to make accurate electrochemical measurements in solutions of low ionic strength because these solutions are nonconductive. Therefore, instead of keeping the ionic strength low, a high concentration of electrolyte is added to keep the ionic strength of analyte solutions high (for conductivity) and *constant*. This constant value of ionic strength assures that the activity coefficient of each ion is constant, thus activity is proportional to concentration and the potential will depend on concentration. This proportionality constant introduced by the activity coefficient becomes part of the slope of calibration curve and need never be officially measured.

In addition to maintaining electrical conductivity, there is a hidden advantage in working with solutions which have high electrolyte concentrations. Since the electrolyte concentration is much higher than the concentration of analyte, small variations in the concentration of analyte will not affect the ionic strength nor its activity coefficient. This results in more accurate calibration curves.

Potentiometric measurements (including pH measurements) are based on a calibration

curve where the signal (E) is graphed against either the log of analyte concentration or p-function of the analyte concentration. The only difference in these graphs is the direction of the slope. See Figure 2. In pH measurements, the calibration curve is stored in the meter when the standardization/calibration buffers are measured.

While a calibration curve is the most common method of analysis for potentiometry, standard addition can also be used. However, using standard addition is more complex for potentiometry than many other techniques (e.g., spectrophotometry) since the signal (E) is not proportional to concentration. Standard addition methods require that the analyst assume a *Nernstian Response*—that the Nernst equation (equation 1) is rigorously followed. When using the Nernst equation with ion selective electrodes, n =charge of the ion.

An *indicator electrode* or, more commonly, *ion selective electrode* (ISE) is an electrode whose potential responds to a specific substance. (Figure 3 shows diagrams of selected indicator electrodes.) These electrodes are selective rather than specific, which means that they might also respond (although with a smaller signal) to other ions, particularly those with similar chemistry. However, these electrodes *are* selective enough that they only respond to one form of the ion. (i.e., different oxidation states, complexation, or acid/base forms will not be detected.) Therefore, to get accurate results, the analyst must take into account the chemistry of the analyte and the matrix of the analyte solution.

For example, fluoride ion is generally measured in the presence of a “total ionic strength adjustment buffer (TISAB).” In addition to a high concentration of electrolyte (~1.0 M NaCl), it contains an acetic acid buffer and EDTA. The sodium chloride is added to maintain constant ionic strength (as discussed above) and maximize conductivity. Despite the similar chemistry,

the solid state fluoride ISE does not respond to chloride ion. If it did, because F^- is in such low concentration (usually ppm) compared to the NaCl, the measured signal would be due to the NaCl rather than the analyte. The acetic acid buffer is added because fluoride ion is a weak base. Therefore it will react, at least partially, with any acid present. The presence of the buffer assures that the *ratio* of F^- to HF is the same for all standards and samples and that the concentration of fluoride ion depends on fluoride ion concentration rather than the extent of the acid-base reaction. As with the addition of electrolyte, rather than eliminate the effect, the acid-base reaction is controlled. Like the activity coefficient, the equilibrium constant and the pH are included in the slope of the calibration curve. The EDTA is added because fluoride ion can act as a ligand. If there are metal ions in the sample matrix, the EDTA will bind preferentially with the metal ion. Thus the signal will not decrease due to reaction of fluoride ions with the metal ion.

Commercial ISEs tend to be categorized as glass, gas sensing, membrane solid state and redox (or ORP) electrodes.

Glass electrodes are commonly used to detect H^+ ions. There is a solution with a constant H^+ activity on the inside of the glass membrane as well as a Ag/AgCl half-cell. On both sides of the hydrated glass, the H^+ interacts with the glass, replacing metal ions in the glass lattice. A difference in the activity of H^+ on either side of the glass creates a potential between the half cell exposed to the internal solution and that of the external solution. The potential difference is due to the charge separation across the glass as opposed to a redox half-reaction.

In addition to H^+ ions, the glass will also interact with sodium ions. While the signal due to sodium is smaller than that due to hydrogen ion, in solutions of high pH, Na^+ concentrations

tend to be high while H^+ concentration are low, so the measured potential may be due to Na^+ rather than H^+ and pH measurements are not accurate. However, by varying the composition of the glass slightly, glass electrodes can be made give a larger signal for sodium ion, thus creating a sodium ion selective electrode!

Gas sensing electrodes respond to dissolved gases in solution . The dissolved gas diffuses across the membrane into a small volume of buffer, specific for each electrode. Reactions of the gas with the buffer causes a pH change sensed by an internal glass pH electrode.

Membrane electrodes have an ion exchange material contained in a solid plastic membrane. The sensed ion is exchanged across the membrane, creating the potential. These operate in a manner similar to a glass electrode, with the plastic membrane instead of the glass.

Solid state electrodes are made of a uniform or homogeneous solid substance which is sensitive to changes in analyte activity. The electrical connection is made directly between this ion sensitive area and the meter. The ion sensitive area is generally a salt containing the ion of interest. For example, the fluoride selective electrode is made with LaF_3 and the chloride selective electrode with $AgCl$.

Combination electrodes combine the reference and indicator electrodes in one electrode body. Most pH electrodes are designed as combination electrodes.

All the above electrodes are based on the development of a *junction potential* which is due to the build up of charge at an interface. A *redox (or ORP for oxidation/reduction potential) electrode* operates on a different mechanism. This electrode measures the reducing or oxidizing power of a solution regardless of the ions which are causing the effect. Thus, it is *not* selective.

The electrode is normally made of platinum, which is electrically conductive without participating in the reaction. Redox electrodes are used to give an overall indication of the reactivity of the solution and are often used to construct titration curves of redox titrations.

Potentiometry has many advantages, the primary one being the range of concentrations over which it is effective. For example, pH electrodes generally work best in the pH range of 2-10. This refers to concentrations between 10^{-2} and 10^{-12} M, a range of 10^{10} ! In addition, the method can be used regardless of the color or turbidity of the solution, is nondestructive and noncontaminating. The method is also very inexpensive, often requiring less than \$1000 to obtain all items necessary for measurements. The on-going expenses are only the calibration standards (which can be reused) and occasionally replacing an electrode. If the meter will work on batteries, this method is also portable to nearly anywhere. On the other hand, the accuracy and precision obtainable from potentiometry is poor. It is not unusual to have relative errors as high as 10%.

Voltammetry. Voltammetry is a series of techniques where potential is controlled and current is measured. In this technique, the current is due to a redox half-reaction induced by the applied potential. The graph of current versus potential, called a voltamogram, provides information about the chemical reaction. It is important that the voltamogram reflect the analyte's reaction at the working electrode. Thus, it is important that the potentials measured be in a region where solvent, electrolyte and electrode are not reacting. This range of potentials is called the *potential window*. The potential windows for various systems are shown in Figure 1.

Cell set-up. Because the changes in current affect the potential (recall Ohm's Law: $E=iR$), voltammetry requires a three electrode configuration as well as the usual highly

conductive analyte/electrolyte solution. The three electrodes are the working electrode, the reference electrode and the auxiliary (a.k.a. “counter”) electrode. The *working electrode* is the electrode where the half-reaction of interest occurs. Ideally, a working electrode allows electron transfer to occur at its surface without participating in the reaction or reacting itself. The *reference electrode* (as usual) maintains a constant potential. The same type of reference electrodes are used in voltammetry as are used in potentiometry. The applied potential is the potential difference between the working and reference electrodes. The *auxiliary electrode* is where the other half of the reaction occurs. The current flowing between the working and the auxiliary electrode is measured.

While the reaction which occurs at the auxiliary electrode is not important to the voltammetric study, it is important that processes occurring at this electrode not determine the overall current. Thus, this electrode should have a large surface area (so that current is not limited by the size of the auxiliary electrode) and be far enough from the working electrode that the reaction occurring at the auxiliary electrode will not interfere with the reaction occurring at the working electrode. Usually a platinum wire or platinum flag electrode is used as a auxiliary/counter electrode.

There are a variety of working electrodes to choose from. The best choice depends on the type of experiment. Classically, most working electrodes were made of mercury. These liquid electrodes are very reproducible, have an easily renewable surface, and work over a wide range of negative (reducing) potentials. Because mercury electrodes work so well under reducing conditions, they were commonly used to detect metal ions. However, due health and environmental concerns, mercury is no longer a popular choice. Voltammetry also moved away

from mercury electrodes due to the interest in biochemical reactions, which tend to occur at positive potentials (where mercury cannot be used). Instead “solid electrodes” made of platinum, gold or carbon are used. These electrodes are relatively inexpensive, reusable and operate within a wide variety of potential windows. Their major disadvantage is that the surface of these electrodes can interact irreversibly with the analyte or contaminants in the solution. This often changes the electrochemical behavior, sometimes blocking the surface and not allowing electron transfer to occur.

Modes of transport (mass transport). Before an analyte can react, it must get to the electrode surface. There are three ways this can occur: migration, convection and diffusion. *Migration* is the movement of a charged body under the influence of an electric field. The large concentration of electrolyte usually keeps this from being an important mode of transport. *Convection* refers to stirring or hydrodynamic transport. With one important exception, most techniques require an quiescent solution, since it is extremely difficult to determine the rate of convection or to keep the rate of convection constant. *Diffusion* is the movement of a species under a concentration gradient. Most electrochemical theory is based on the assumption that the system is diffusion-controlled. In some instances, however, the analyte is highly attracted to the electrode and will *adsorb*, i.e., attach itself to the surface of the electrode. Molecules which are adsorbed will not show a mass transport effect. However, many analytes will both adsorb and diffuse, in which case an averaged effect is observed.

Thermodynamics and Kinetics. Since potential is related to both concentration and potential energy of the reactants and products, it is primarily a thermodynamic measurement. It is characteristic of the reaction and concentration. While the concentration relationship is of

primary importance in potentiometry, potential is generally used to characterize the reaction in voltammetry. *Formal potential* ($E^{\circ'}$) is the potential when the concentration of the analyte and its product are equal under conditions of the experiment. It is commonly used to characterize the thermodynamics of the reaction, since the effect of analyte concentration is removed. It is similar in concept to the standard potential, E° , except that $E^{\circ'}$ can be used for any set of conditions not just when all activities are unity. Note: Biochemists define a specific set of conditions (biological conditions, pH = 7) for formal potential, electrochemists are more flexible.

On the other hand, current, which measures of the instantaneous rate of reaction, is very much a kinetic measurement. Since rate will depend on concentration, current can be (and is) often used to determine concentration, provided other factors which affect rate are kept constant. Factors which will affect the rate include the usual chemical ones, such as temperature and the reaction mechanism, as well as factors which are unique to electrochemistry. Since all electrochemical reactions occur at the electrode surface, the rate depends on the surface area of the electrode. If there is more surface, more analyte can react at any given time and the current increases proportionally. In addition, since the analyte must reach the surface to react, the rate/current will depend on the rate at which the analyte can reach the surface. A reaction which is chemically fast enough that the mode of transport is the limiting step is called “reversible” while a reaction where a step in the mechanism (such as electron transfer) is the rate-determining step is “irreversible.” Note: “Electrochemical reversibility” which refers to the kinetics of the process is often confused with “thermodynamic reversibility” or “chemical reversibility” which refers to the ability of the products to return to reactants. It pays to be very clear about which of the two is meant when describing a process as “reversible” or “irreversible.”

Linear Sweep Voltammetry (LSV). In LSV, potential is changed at constant rate while the current is measured. The rate at which the potential changes is called the scan rate (v) and typically has values between 1 mV/s and 1 V/s. With both potential and current, positive and negative values are used to reflect direction—oxidation or reduction—and measure the electron flow or potential difference between two electrodes rather than as an absolute measurement. Traditionally, the potential is shown on the x-axis with more negative (reducing) potentials to the *right*. Recently voltammograms have been shown in a more standard fashion (with positive values on the right), since that is easier with graphing programs. Currents are graphed on the y-axis with currents due to reduction assigned positive values. Currents due to oxidation appear as negative values.

The sweep is begun at a potential where no reaction occurs. If this potential is not known, the scan could be started at the negative end of the potential window for an oxidation or the positive end of the window for a reduction. Initially, there will be a slight increase in current due to background and/or capacitive current. As the potential approaches a value where the half-reaction of the analyte begins to occur, the current will substantially increase. It will continue to increase until all the analyte at the surface of the electrode has reacted. Since analyte must now diffuse to electrode to react, the surface concentration and therefore the current, decreases somewhat. When the analyte has been depleted from the volume around the electrode, the concentration of reacting analyte will depend solely on diffusion and the current will reach a constant value. (See Figure 4.)

In LSV, it is typical to measure the *peak current* (i_p), the largest current; *peak potential* (E_p), the potential at the peak current and the *half-peak potential* ($E_{1/2}$), which is the potential

when the current is half of the peak current. The half-peak potential is sometimes called the *half-wave potential*. The determination of each of these is shown in Figure 4.

The peak potential is characteristic of the system being studied. It is primarily a thermodynamic measurement, but may be affected by the kinetics of the system. Because the applied potential continues to change, even as the reaction occurs, the measured peak potential will be more negative (for reduction) or more positive (for oxidation) than thermodynamics require. The deviation from theoretical is even larger if the kinetics of the reaction are slow. The kinetic slowing could be due to the rate of electron transfer itself or the mass transport of the analyte. Thus, the half-peak potential, which shows fewer kinetic effects, rather than the peak potential is more commonly used to describe energetics of the system. Theoretically, the formal potential is the same as the half-peak potential and the two terms are often used interchangeably.

The value of the peak current depends on several factors including the concentration of analyte, kinetics of electron transfer and the mass transport of the analyte. In a system where diffusion is the only mode of mass transport (diffusion-controlled) and the kinetics of electron transfer are fast (reversible), the relationship is

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C^* \quad (4)$$

where i_p is the peak current(A), n is the number of electrons transferred (mol e/mol analyte), A is the area of the electrode (cm^2), D is the diffusion coefficient (cm^2/s), v is the scan rate (V/s) and C^* is the bulk concentration of analyte ($\text{mol analyte}/\text{cm}^3$). The dependence on bulk concentration (rather than concentration at the electrode surface) allows peak current to be used for quantitative measurements.

In electrochemistry, voltammograms (the graph of current versus potential) are generally

used in the same way spectra (especially uv-vis spectra) are used in spectroscopy. In both cases, the pattern is a qualitative picture of the system and its interaction with energy. In spectroscopy, the interaction is with energy in the form of light; in voltammetry, the interaction is with electrochemical potential. In spectroscopy, the intensity of the signal (absorbance or emission) at the maximum wavelength can be related to concentration. In the same way the maximum intensity of the signal, peak current, is also proportional to concentration. Both full spectra and voltammograms are generally used for qualitative rather than quantitative measurements.

Linear Sweep Voltammetry at a Rotating Disk Electrode (LSV at RDE) aka

Hydrodynamic Voltammetry. In this variation, the solution is stirred by rotating the working electrode at a constant rate. The voltammogram is basically the same as with unstirred solutions, in that there is a constant background current until the sweep reaches a potential where the reduction (or oxidation) begins to occur. The current sharply increases until the reaction reaches a maximum rate. Unlike the quiescent solution, however, the analyte around the electrode is constantly being replenished by the stirring of the solution so the current does not decrease. (See Figure 5.) This maximum current is called the limiting current (i_l). The limiting current is proportional to the concentration of analyte according to the Levich equation

$$i_l = 0.620nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C^* \quad (5)$$

where i_l = limiting current (A), n = number of electrons transferred (mol e^- /mol analyte), F = Faraday's constant (96,484 C/mol e^-), A = area of the electrode (cm^2), D = diffusion coefficient of analyte (cm^2/s), ω = rate of rotation of working electrode (s^{-1}), ν = scan rate (V/s) and C^* = bulk concentration of analyte (mol/cm^3). Formal potentials are determined by measuring the half-wave potential ($E_{1/2}$).

An interesting application of RDE is to obtain information about the kinetics of the redox reaction. As the rate of electrode rotation increases, the analyte will spend less time at the electrode surface. Reactions, or reaction steps, which take a reasonably long time to occur will be observed at slow rotation rates but not observed at fast rotation rates. For example, consider a process which involves the transfer of two electrons, where the first electron is quickly transferred and the second more slowly. At fast rotation rates, $i_1/\omega^{1/2}$ will be half of $i_1/\omega^{1/2}$, since only the first electron transfer is observed ($n=1$ instead of $n=2$). The rate of the second electron transfer can be determined from the rate of electrode rotation.

Linear Sweep Voltammetry at a Dropping Mercury Electrode (DME) aka Polarography.

A dropping mercury electrode consists of a capillary through which mercury is forced. At the end of the capillary, a drop of mercury, which acts as the working electrode, slowly forms, increases in size and then drops off to be replaced by another. The potential is still applied in a linear sweep which is not related to the drop rate.

As the drop grows, the current increases. This increase is due to the increase in electrode area rather than a redox current. When the drop falls off, the current sharply decreases, although not to zero since another drop immediately forms and current increases again. The redox current is superimposed over this fluctuation. This dropping action also stirs the solution, so that the concentration of analyte (as the drop begins to form) is the same as in the bulk solution. Consequently, as with RDE, there is no decrease in current due to depletion of analyte around electrode. In fact, the voltamogram (Figure 6) has essentially the same pattern as with RDE and the maximum current is also called the limiting current. With DME, however, the limiting current is related to concentration by the Ilkovic equation

$$i_l = 708nD^{1/2}C^*m^{2/3}t^{1/6} \quad (6)$$

where i_l = limiting current (A), n = number of electrons transferred (mol e^- /mol analyte), D = diffusion coefficient of the analyte (cm^2/s), C^* = concentration of analyte in bulk solution (mol/cm^3), m = rate of mercury flow (mg/s), t = lifetime of drop (s).

Polarography was one of the first quantitative instrumental techniques. It has excellent detection limits (around 10^{-6} M) and good precision (about 1%). Polarography is primarily used in the quantitative detection of metal ions, since these can be reduced in mercury's potential window. It has the advantage over techniques like atomic absorption spectroscopy of being able to differentiate between different oxidation states of the metal, since each oxidation state will be reduced at a different potential. While used extensively many years ago, due to health and environmental concerns about mercury and the advancement of many other types of instrumentation, it is rarely used today.

Cyclic Voltammetry (CV). The most common type of electroanalytical measurement is cyclic voltammetry. This technique consists of a linear sweep which is then reversed in direction, so that the products of the forward sweep react in the reverse sweep. Peak potentials and currents are measured and designated E_{pa} (anodic peak potential) and i_{pa} (anodic peak current) for the negative to positive sweep and oxidation of the analyte and E_{pc} (cathodic peak potential) and i_{pc} (cathodic peak current) for the positive to negative sweep and the reduction. Figure 7 shows a typical cyclic voltammogram and measurements for a fast, thermodynamically reversible reaction.

Cyclic voltammetry is a useful technique for obtaining substantial information about the electrochemical processes. Thermodynamic information is related to the formal potential. With

CV, the formal potential is calculated from the average of the peak potentials

$$E^{\circ'} = (E_{pa} + E_{pc})/2 \quad (7)$$

The formal potential allows a comparison of the energetics of different systems. It is specific for the system studied, but is not dependent on the concentration of the substance studied.

Cyclic voltammetry is also very useful in determining the mode of transport for the system. The system is designed so that there are two possible modes of transport, adsorption and diffusion. The system might exhibit either of these or a combination of both. In an adsorption-controlled system, the analyte does not have to travel to the electrode. Thus, when the potential required for reaction is reached, the current increases and decreases much more rapidly. The result is a sharp (narrow) peak with a high current (since all the analyte can react at once). Also because of this quicker reaction, the anodic and cathodic peaks are closer than in a diffusion-controlled system. See Figure 8.

A more quantitative method for determining the mode of transport can be accomplished by varying the scan rate (v). For diffusion-controlled reactions, the peak current (i_p) is proportional to $v^{1/2}$ (see equation 4). For an adsorption-controlled reaction, i_p is proportional to v according to

$$i_p = (n^2 F^2 / 4RT) v A G^* \quad (8)$$

where i_p = peak current (A), n = number of electrons, F = Faraday's constant, R = gas constant (J/mol·K), T = temperature (K), v = scan rate (V/s), A = area of electrode (cm²), G^* = mol of analyte adsorbed on the electrode (mol/cm²). Since a major (and measurable/controllable) difference between equations 4 and 8 is the exponent on scan rate, the other factors can be removed by graphing $\log i_p$ (y-axis) versus $\log v$ (x-axis). Thus, the slope of this line will be the

exponent on the scan rate. If this graph ($\log i_p$ v. $\log v$) has a slope of 0.5, the process is diffusion-controlled. If the graph has a slope of 1.0, the process is adsorption-controlled. If the slope is between 0.5 and 1.0, both processes are important.

Kinetic information can also be obtained from cyclic voltammetry. The most useful calculation for kinetic information is ΔE_p , where

$$\Delta E_p = E_{pa} - E_{pc} \quad (9)$$

In fast/reversible reactions, the formal potential will be determined by the thermodynamics. However, the mode of transport will determine how far from the formal potential the peak actually occurs. This is because by the time the analyte reaches the electrode, the scan has already gone beyond the formal potential. If the reaction is slow, the rate of reaction will also affect the position of the peak, since the reactants not only have to reach the electrode, but also will not immediately react once there. The rate of this reaction is measured in terms of the “heterogeneous rate constant (k_s).” This rate constant is “heterogeneous” because it refers to the rate of electron transfer between the analyte in solution and the electrode (solution phase to solid phase). For adsorption-controlled reactions, no transport to the electrode is needed, so the peak potential depends only on thermodynamics. Thus ΔE_p is used to evaluate the rate of reaction as follows.

If both the forward and reverse reactions are reversible (fast) and adsorption-controlled $E_p = E^\circ$ for both the anodic and cathodic peaks, and $\Delta E_p=0$. In reversible, diffusion-controlled reactions, the maximum rate of reaction (i_p) will not be reached until the potential sweep is beyond the formal potential, thus the cathodic peak is more negative than the formal potential and the anodic peak is more positive than the formal potential. Theoretical calculations show

that if diffusion controls the rate of reaction $\Delta E_p = 59/n$ mV, where n is the number of electrons transferred, and that this value of ΔE_p is independent of scan rate. If the reaction itself is slow, the sweep will continue even further before the maximum rate of reaction is reached. Thus, the faster the scan rate, the greater the value of ΔE_p . Therefore, any $\Delta E_p > 59/n$ mV and which increases with increasing scan rate shows it is that the rate of electron transfer rather than diffusion is the rate-limiting step. Systems where $\Delta E_p > 200$ mV are called “irreversible.” Systems where $\Delta E_p = 60-200$ mV are called “quasi-reversible.” Most analyses used for reversible systems will give acceptable results for quasi-reversible systems too. R.S. Nicholson determined the relationship between ΔE_p and the heterogeneous rate constant, k_s , for quasi-reversible systems. This relationship is shown in Figure 9.

It is also possible to get qualitative mechanistic information from cyclic voltammetry. For reactions at electrodes, the mechanistic step may or may not involve an electron transfer. Steps which consist of the gain or loss of an electrons are labeled “E”; steps which consist of atom rearrangement (like gain or loss of H^+) are labeled “C.” When the chemical step precedes the electron transfer, this is often called a “CE mechanism,” whereas when the electron transfer precedes the chemical step it is a “EC mechanism.” Changing scan rate will affect peak currents of the forward and reverse reaction differently, depending on the mechanism. Using data from Nicholson and Shain, the type of mechanism can be determined by studying the change in the ratio of peak currents (i_{pa}/i_{pc}) with changes in scan rate. See Figure 10.

Many electrochemical reactions involve the transfer of more than one electron. This second electron transfer is sometimes observed as a second peak. The second peak is observed when the energy (E) required for the second electron transfer is greater than for the first. If that

is not the case, then when the first electron transfer occurs, there is already sufficient energy for the second electron transfer so it occurs immediately. Thus, a second peak is not observed. This second electron shows up in the magnitude of the peak current ($i_p \propto n$). In addition to a second electron transfer, there may also be more chemical steps resulting in mechanisms of ECEC, EECC, CECE, etc. Interpretation of voltammograms with such mechanisms are beyond the scope of this class.

Pulse Techniques. In sweep techniques, the potential gradually and consistently changed. However, in a pulse techniques the initial potential (where no reaction occurs) is directly changed to the final potential (where the reaction rate is at maximum). Hence it is referred to as a step or pulse instead of a sweep. Because there are only two potentials, the signal is graphed as a function of time rather than potential. The appropriate initial and final potentials are normally determined using voltammetry. The initial potential (E_i) should be a value before the peak begins and the final potential (E_f) at a value in the diffusion-limited region, when the current levels off after the peak.

Chronoamperometry. In chronoamperometry, current is graphed as a function of time, using the same three-electrode cell configuration as with voltammetry. A typical response is shown in Figure 11. At the initial potential, there is only background current. When the potential is pulsed, the reaction quickly reaches its maximum value to decrease exponentially as the analyte at the electrode surface is depleted. The relationship between current and time is expressed by the Cottrell Equation

$$i = nFAD^{1/2}C^*\pi^{-1/2}t^{-1/2} \quad (10)$$

where i = current (A), F = Faraday's constant (C/mol e^-), A = area of the electrode (cm^2), D = diffusion coefficient (cm^2/s), C^* = concentration of analyte in the bulk solution (mol/cm^3), t = time (s).

Chronocoulometry. When the current obtained in a chronoamperometric experiment is integrated, the technique then becomes "chronocoulometry" (since charge is the integral of current). One of the useful aspects of this integration is that time-dependent processes (diffusion) are separated from non-time dependent processes (adsorption and background/capacitive

current). The relationship between charge and time is expressed with the integrated Cottrell Equation

$$Q = 2nFAD^{1/2}C^*\pi^{-1/2}t^{1/2} + nFA\Gamma + Q_{dl} \quad (11)$$

where Q = charge (C), n = number of electrons transferred (mol e^- /mol analyte), F = Faraday's constant (96,484 C/mol e^-), A = area of the electrode (cm^2), D = diffusion coefficient of analyte (cm^2/s), C^* = concentration of bulk solution (mol analyte/ cm^3), t = time (s), Γ = mol of adsorbed analyte (mol analyte/ cm^2), Q_{dl} = charge of double layer (C) which is from your background current. From the integrated Cottrell equation, chronocoulometry is most easily analyzed by graphing Q (y-axis) versus $t^{1/2}$ (x-axis), which will give a straight line. With careful choice of electrochemical cell, this experiment can be used to determine many useful pieces of information.

A common use of chronocoulometry is the determination of the area of the electrode. Because this method takes into account any surface irregularities, it is more accurate than measuring the area geometrically. This experiment requires a well-characterized electrochemical reaction. The one most commonly used is the reaction between ferricyanide ($\text{Fe}(\text{CN})_6^{3-}$) and ferrocyanide ($\text{Fe}(\text{CN})_6^{4-}$) ions.



The diffusion coefficients of both ferricyanide ion and ferrocyanide ion at solid electrodes have been well-characterized by Stackelberg, et al.¹ Ferricyanide has a value of $7.63 \times 10^{-6} \text{ cm}^2/\text{s}$ in 0.1 M $\text{KCl}_{(\text{aq})}$. Using the integrated Cottrell equation (equation 11), the area of the electrode is

¹von Stackelberg, M.; Pilgram, M.; Toome, V. *Z. Elektrochem.*, **1953**, 57, 342.

determined from the slope of Q v. $t^{1/2}$ for a known concentration of ferricyanide in 0.1 M $KCl_{(aq)}$, since all values except electrode area are known for that system. Careful attention to units is required for a correct value (see equation 11), thus it is often of value to first estimate the area geometrically to compare with the more exact value from chronocoulometry.

Another common use of chronocoulometry is to determine the diffusion coefficient of an analyte. The diffusion coefficient is also determined from the slope of the graph of Q vs. $t^{1/2}$ and an electrode of known area. This method is especially valuable (as compared to chronoamperometry or voltammetry) for determining diffusion coefficients because kinetic and adsorption effects have been moved into the y-intercept by the integration.

A third common use of chronocoulometry is to determine the amount of analyte adsorbed on the electrode (Γ). This value is determined from the y-intercept of the graph of Q v. $t^{1/2}$. The y-intercept value contains terms for both the charge due to adsorbed analyte and charge due to background current. However, the background current is easily accounted for with the chronocoulometry of a blank solution. The y-intercept of the Q v. $t^{1/2}$ graph of the blank would be Q_{dl} . This value can then be subtracted from the y-intercept of the chronocoulometry of your analyte, thus

$$\text{y-intercept of analyte solution} - \text{y-intercept of blank} = nFA\Gamma \quad (13)$$

and, from this, Γ is easily determined algebraically.

List of Figures and Tables.

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From Orion's Electrochemical Handbook p. 55 & 56

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Figure 10. Variation in the ratio of anodic to cathodic peak currents as a function of scan rate for several electrode processes with reversible electron transfer. from Nicholson and Shain, *Anal. Chem.* **1964**, 36, 706.

Figure 11. Chronoamperometry. (A) potential excitation signal where E_i = initial potential (where no reaction occurs) and E_s = final potential (redox reaction at maximum rate) (B) Current-time response signal (chronoamperogram). From Kissinger, P.T; Heineman, W.R. *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker: New York, 1984, p. 56.

Glossary

adsorption—to hold molecules at the surface of a solid

anode—electrode at which oxidation occurs

background current—current not due to chemical reaction of the analyte

capacitive current—background current due to the electrode acting as a capacitor and becoming charged.

cathode—electrode at which reduction occurs

charge—measure of the number of electrons, unit normally coulombs (C); note: $96,484 \text{ C} = 1$ mole of electrons

charging current—see capacitive current

current—rate of flow of electrons, unit normally amperes (A)

diffusion—movement through solution due to a concentration gradient

electrochemical potential—see “potential”

electrolyte—substance which forms ions in solution which do not participate in the reaction of interest but are in sufficient quantity to make the solution electrically conductive

formal potential (E_f)—potential when the concentration of the substance being oxidized is equal to the substance being reduced; it is characteristic of the system under study; customarily measured with the half-wave potential in LSV and with the average of the peak potentials in CV

half-cell—one half of an electrochemical cell containing an electrode, an electrically conductive solvent system, analyte and a salt bridge connection

half-wave potential ($E_{1/2}$)—potential at half of the peak or limiting current; a measure of formal potential

indicator electrodes—electrodes used in potentiometry whose potential depends on the activity of analyte

ion selective electrode (ISE)—electrode used in potentiometry which gives a potential signal in the presence of the ion for which it is selective

Levich equation—expression for limiting current in LSV with a rotating disk electrode; equation 5

linear sweep voltammetry (LSV)—measuring current as the potential is systematically changed (linearly increased or decreased)

migration—movement through a solution due to a potential gradient

Nernst Equation—relationship between potential and concentration

$$E = E^\circ + RT/nF \ln([\text{ox}]/[\text{red}])$$

Nernstian Response-- the a response which follows the Nernst equation. A Nernstian response at room temperature would have a slope of about $60/n$ mV when potential vs log [analyte] is graphed. n = the charge in potentiometry or number of electrons transferred when a redox reaction is involved.

normal hydrogen electrode (NHE)—half-cell consisting of a platinum black (platinized platinum foil) electrode, one atm H_2 gas and H^+ at an activity of 1. Its electrode potential is defined as zero volts.

peak current (i_p)—the largest current, either anodic or cathodic, which is measured in a voltammogram.

peak potential (E_p)—the potential when the anodic or cathodic current is at maximum

polarography—linear sweep voltammetry at a dropping mercury electrode

potential (also electrochemical potential)—measurement of energy of an electrochemical reaction

potential window—range of potentials for a given solvent/electrode system where analytical measurements can be made

reference electrode— half-cell with known, constant electrochemical potential; unit normally volts (V)

salt bridge— a connection between two solutions which allows electrical conductivity to be maintained without mixing of solutions; traditionally containing a high concentration of salt (often in an agar matrix) but can be as simple as a glass frit

saturated calomel electrode (SCE)—reference electrode of liquid mercury and Hg_2Cl_2 in a saturated solution of aqueous potassium chloride. Its potential is +0.241 V v. NHE.

silver/silver chloride electrode—reference electrode of a silver wire coated with silver chloride

and submerged in a saturated solution of aqueous potassium chloride. Its potential is +0.197 V v. NHE.

scan rate (v)—rate at which potential is changed in a voltammetric experiment.

standard hydrogen electrode (SHE)—see normal hydrogen electrode

List of Equations

Constants and Variables used

R = gas constant; 8.314 J/K	T = temperature (K)
n = moles of electrons transferred	F = Faraday's constant; 96,484 C/mol of e ⁻
E = potential (V)	i = current (A)
Q = charge (C)	t = time (s)
[ox] = activity of oxidized substance	m = flow rate of mercury (mg/s)
[red] = activity of reduced substance	ω = rate of electrode rotation (1/s)
v = scan rate (V/s)	Γ = adsorbed analyte (mol/cm ²)
Q _{dl} = background charge (C)	A = area of electrode (cm ²)
D = diffusion coefficient of analyte (cm ² /s)	
C* = concentration of analyte in bulk solution (mol/cm ³)	

Important equations assuming the half-reaction of ox + ne⁻ → red

Nernst Equation

$$E = E^\circ + RT/nF \ln([ox]/[red])$$

at 25°C $E = E^\circ - 0.059/n \log([red]/[ox])$ (note: E is in volts)

Equation for peak current of a reversible LSV

Levich Equation (RDE)

$$i_l = 0.620nFAD^{2/3}\omega^{1/2}v^{-1/6}C^*$$

Ilkovic Equation (DME)

$$i_l = 708nD^{1/2}C^*m^{2/3}t^{1/6}$$

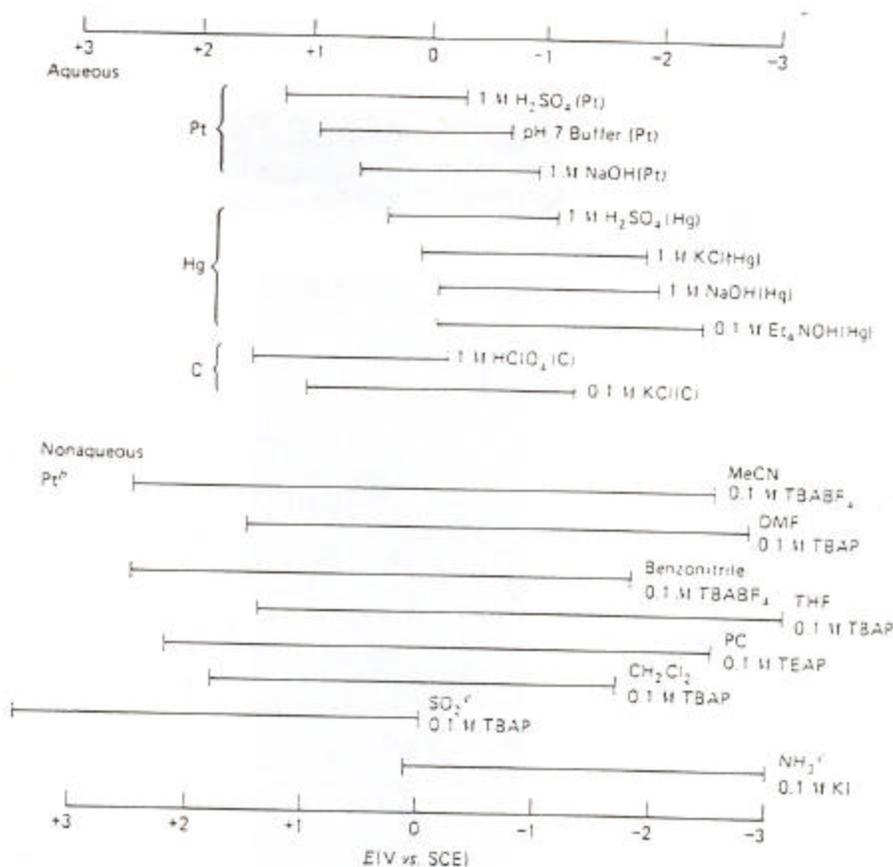
Cottrell Equation (CA)

$$i = nFAD^{1/2}C^*\pi^{-1/2}t^{-1/2}$$

Integrated Cottrell Equation (CC)

$$Q = 2nFAD^{1/2}C^*\pi^{-1/2}t^{1/2} + nFA\Gamma + Q_{dl}$$

Figure 1. Potential Windows of Common Electrode/Solvent Systems
 from Bard, A.J.; Faulkner, L.R. *Electrochemical Methods: Fundamentals and Applications*, J. Wiley & Sons: New York, 1980, back cover.



^a While "voltage limits" and "potential range" are not precisely defined terms, they generally correspond to the useful working range of a solvent for background currents below a few $\mu\text{A}/\text{cm}^2$. For nonaqueous solvents the range is critically dependent on purity and especially on elimination of traces of water. For other compilations of potential range data, see: (1) R. N. Adams, "Electrochemistry at Solid Electrodes," M. Dekker, Inc., New York, 1969, pp. 19-37. (2) C. K. Mann, *Electroanal. Chem.*, 3, 57 (1969). (3) D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists," Wiley-Interscience, New York, 1974, pp. 60-74, 170-171.

^b Range at Hg is usually slightly greater in negative direction, but is limited by oxidation of mercury (at $\sim +0.3$ to $+0.6$ V) in positive direction.

^c Aq. SCE cannot be used in these solvents. Range vs. SCE estimated from measurements vs. Ag/Ag⁺ reference electrode and appropriate reference redox system.

Figure 2. Potentiometric Calibration Curve for Fluoride

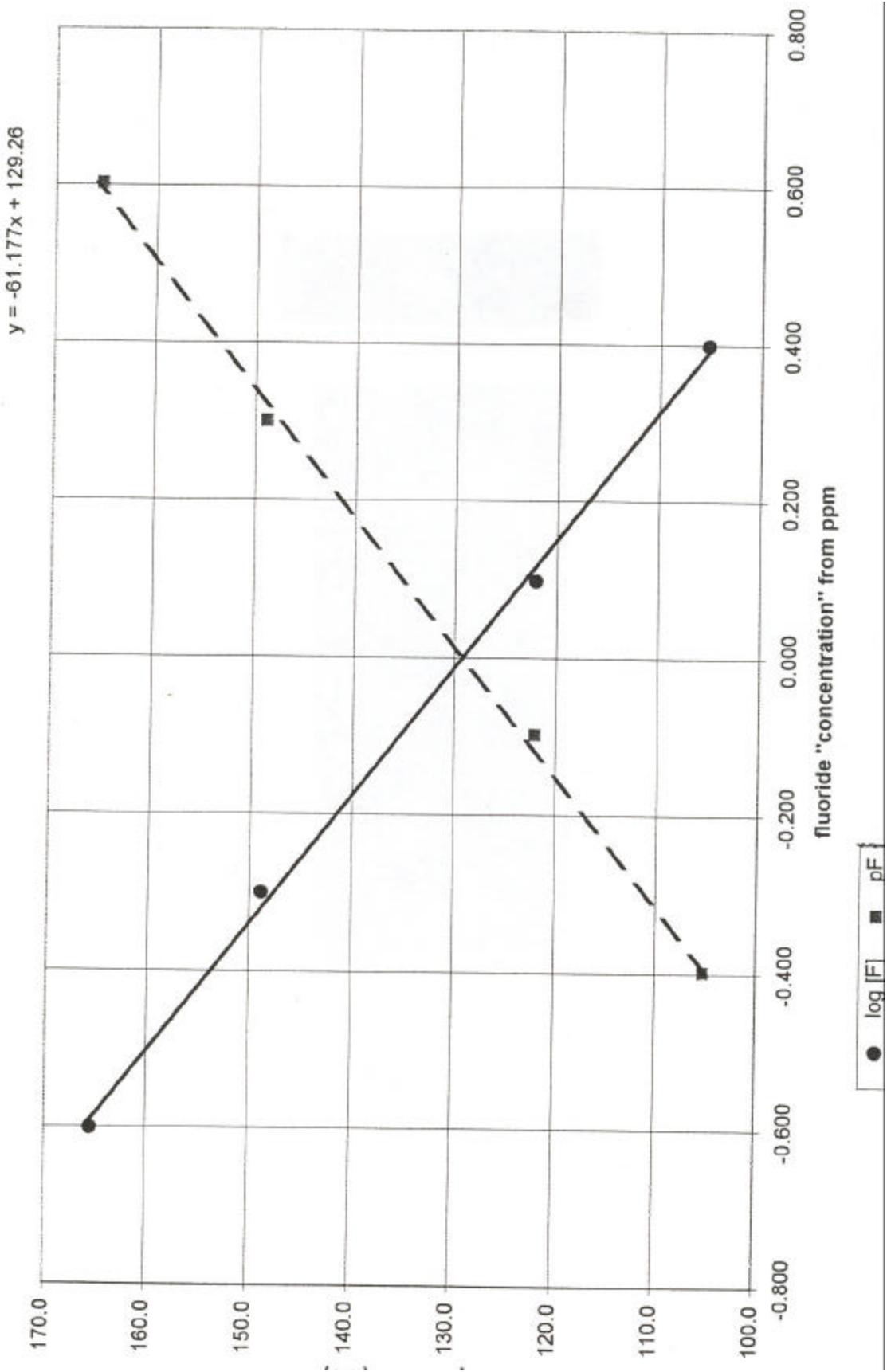


Figure 3. Diagrams of Common Indicator Electrodes
 from *Thermo Orion Laboratory Products Catalog*, Thermo Orion: Beverly, MA, 2001
 pp. 55-56.

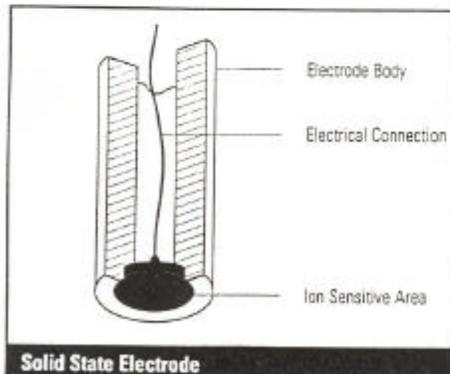
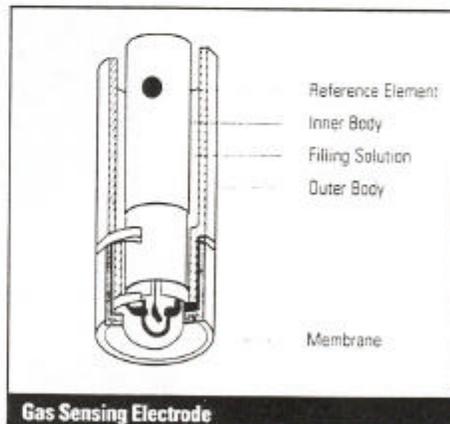
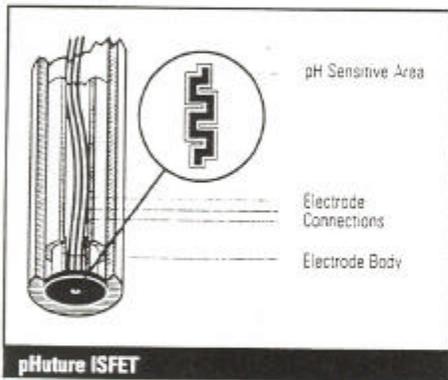
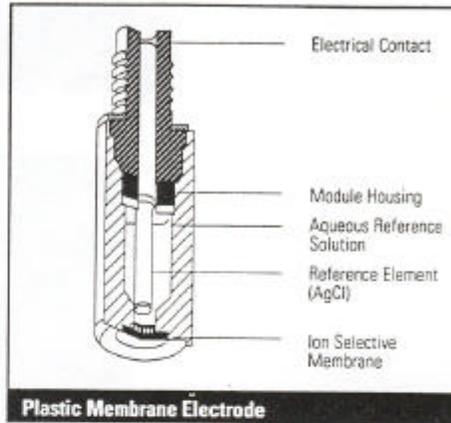
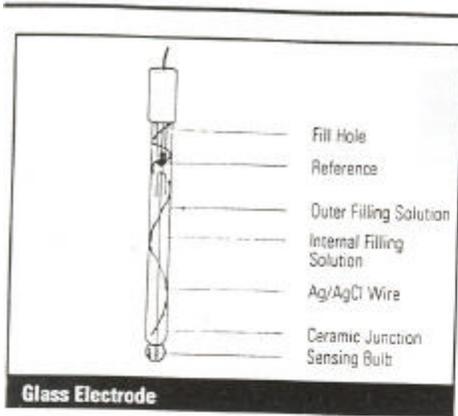


Figure 4. Linear Sweep Voltamogram from Kissinger, P.T.; Heineman, W.R. *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker: New York, 1994, p. 80.

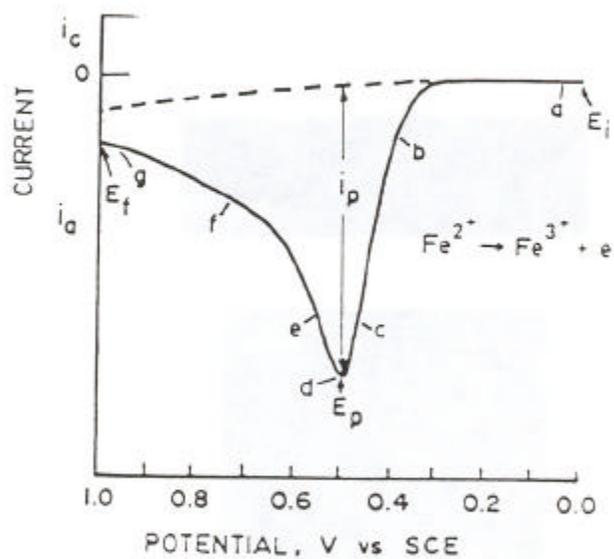


Figure 5. Linear Sweep Voltammetry at a Rotating Disk Electrode aka a Hydrodynamic Voltammogram. (Skoog Figure 25-5)

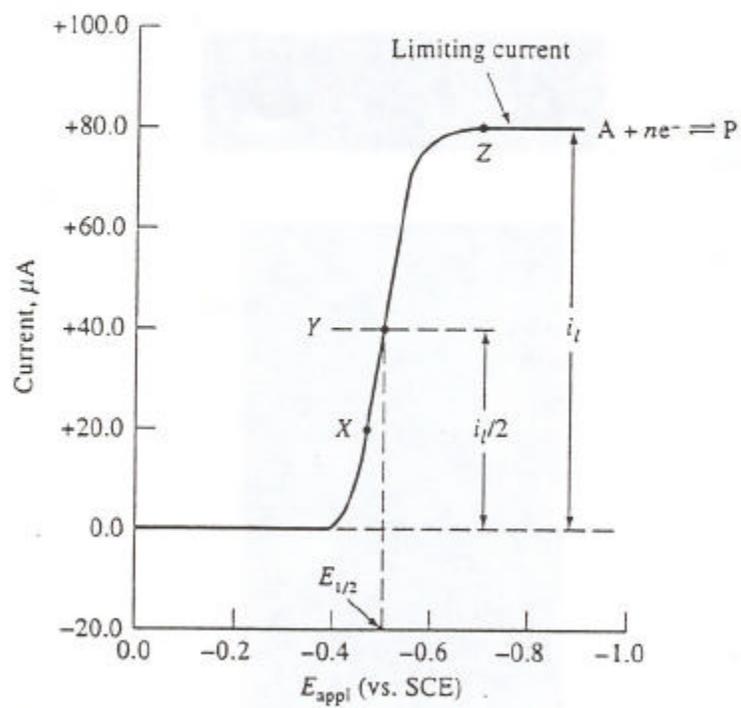


Figure 6. Linear Sweep Voltammetry at a Dropping Mercury Electrode/Polarography. a) current increase due to increase in drop size b) current decrease due to falling drop c) limiting current (Skoog 25-23)

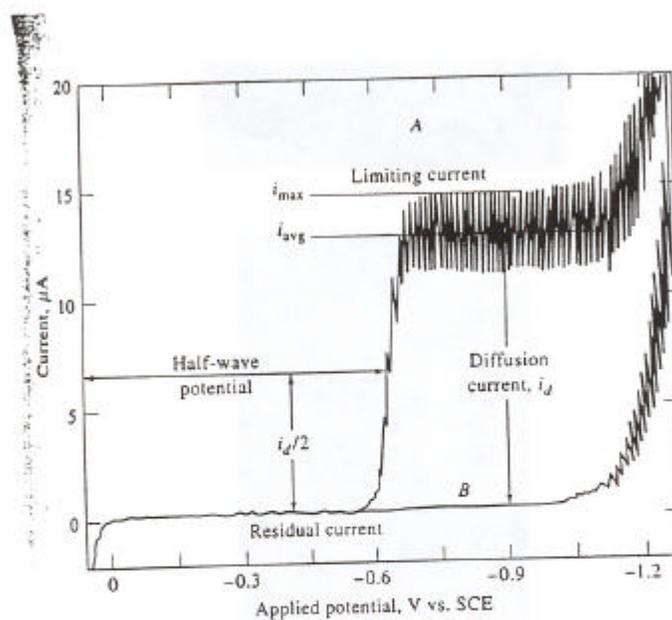


Figure 25-23 Polarograms for (A) a 1 M solution of HCl that is 5×10^{-4} M in Cd^{2+} and (B) a 1 M solution of HCl. (From D. T. Sawyer, A. Subkowiak, and J. L. Roberts Jr., *Experimental Electrochemistry for Chemists*, 2nd ed., p. 59. New York: Wiley, 1995. Reprinted by permission of John Wiley & Sons, Inc.)

Figure 7. Cyclic Voltammogram of a Reversible, Diffusion-Controlled System. E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential, i_{pa} = anodic peak current, i_{pc} = cathodic peak current (Skoog 25-20)

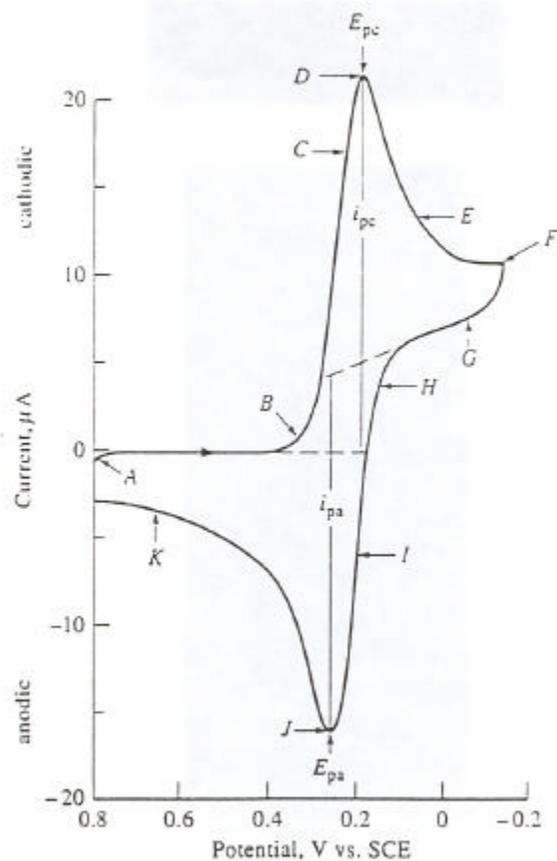


Figure 25-20 Cyclic voltammogram for a solution that is 6.0 mM in $\text{K}_3\text{Fe}(\text{CN})_6$ and 1.0 M in KNO_3 . (From P. T. Kissinger and W. H. Heineman, *J. Chem. Educ.*, 1983, 60, 702. With permission.)

Figure 8. Cyclic Voltammogram of a Reversible, Adsorption-Controlled System.
 From Bard, A.J.; Faulkner, L.R. *Electrochemical Methods: Fundamentals and Applications*,
 John Wiley and Sons: New York, 1980, p. 524.

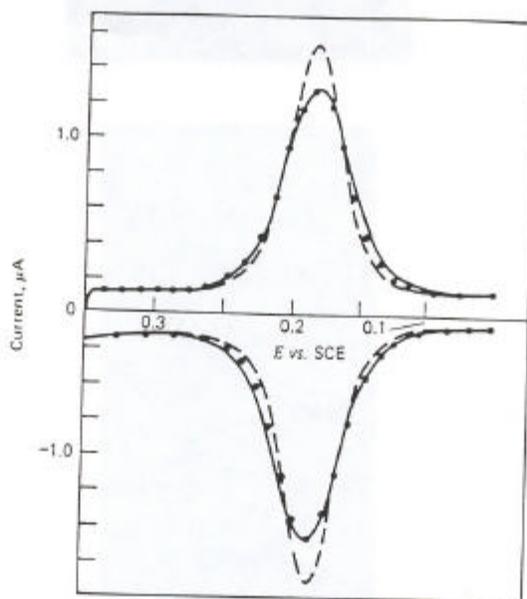


Figure 12.5.2
 Experimental and theoretical cyclic voltammograms for reduction and reoxidation of 9,10-phenanthrenequinone irreversibly adsorbed on a pyrolytic graphite electrode. $\Gamma_0 = 1.9 \times 10^{-10}$ mol/cm²; $\nu = 50$ mV/sec in 1 M HClO₄. (—) experimental voltammogram; (---) theoretical voltammogram calculated from (12.5.11); (●) calculated including nonideality parameters. [Reprinted with permission from A. P. Brown and F. C. Anson, *Anal. Chem.*, 49, 1589 (1977). Copyright 1977, American Chemical Society.]

Figure 9. (A) Cyclic voltammograms exhibiting electrochemical (a) reversibility—1.00 mM Fe^{3+} in 1.0 M HCl, 1.0 M CaCl_2 and (b) irreversibility—1.00 mM Fe^{3+} in 1.0 M H_2SO_4 . (B) Dependence of ΔE_p on k_s and v ($\alpha = 0.5$). From R. S. Nicholson, *Anal. Chem.* 1965, 37, 667.

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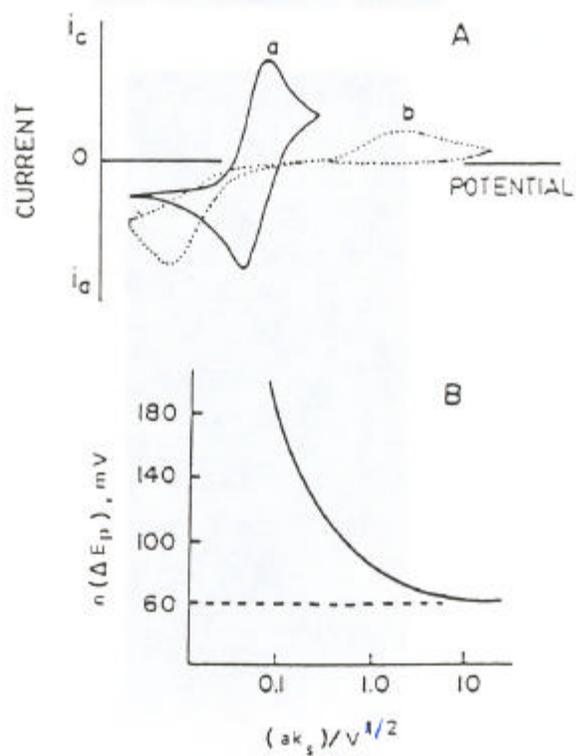
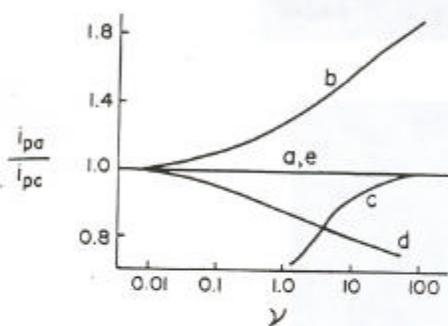


Figure 10. Variation in the ratio of anodic to cathodic peak currents as a function of scan rate for several electrode processes with reversible electron transfer. from Nicholson and Shain, *Anal. Chem.* 1964, 36, 706.

Large-Amplitude Controlled-Potential Techniques



- | | |
|---------------------------------|---------------------------------|
| a. Reversible electron transfer | E: $O + e \rightleftharpoons R$ |
| b. Preceding chemical reaction | C: $Z \rightleftharpoons O$ |
| | E: $O + e \rightleftharpoons R$ |
| c. EC mechanism | E: $O + e \rightleftharpoons R$ |
| | C: $R \rightarrow Z$ |
| d. EC mechanism | E: $O + e \rightleftharpoons R$ |
| | C: $R \rightleftharpoons Z$ |
| e. Catalytic regeneration | E: $O + e \rightleftharpoons R$ |
| | C: $R + Z \rightarrow O$ |

