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AN INTRODUCTION TO ELECTROANALYSIS

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In recent years there has been considerable progress made in the field of electrochemistry. Many new electroanalytical techniques have been developed, as have the advanced instruments required to accomplish them. These activities reflect resurgent interest in a relatively old field which is outlined historically on the inside cover.

The purpose of this booklet is to summarize the more important electroanalytical techniques in use today with regard to their principles, instrumentation, and application. The following references can be considered as primary sources for nearly all phases of this field. In addition, a detailed bibliography is carried at the end of this booklet. It includes a list of references specific to each of the techniques described in the booklet. They will be useful for more intensive study of each technique.

PRIMARY SOURCES OF INFORMATION

1. Delahay, P., *New Instrumental Methods in Electrochemistry*. New York: Interscience, 1954.

2. Hampel, C. A., *The Encyclopedia of Electrochemistry*. New York: Reinhold, 1964.

3. Kolthoff, I. M. and P. J. Elving, *Treatise on Analytical Chemistry*, Part I. Vol. 4, Sec. D-2, Ch. 42-52. New York: Interscience, 1963.

4. Lingane, J. J., *Electroanalytical Chemistry*, 2nd Ed. New York: Interscience, 1958.

5. Meites, L., *Handbook of Analytical Chemistry*, Sec. 5. New York: McGraw-Hill, 1963.

SECTION 1...INSTRUMENTATION PRINCIPLES

The Electroscan 30™ Electroanalytical System was developed to carry out a variety of current-voltage measurements for electrochemical analysis. With the proper cells and electrodes, the Electroscan 30 can be used for at least fifteen electrometric analytical techniques. These various measurements are achieved by using the system as (a) a pH meter (b) a galvanostat, and (c) a potentiostat. The recording function is accomplished by a high-impedance, fast-response, potentiometric recorder which is built into the system. These basic capabilities of the Electroscan 30 are briefly described here. A more detailed instrument description is available in Bulletin 7076, *Beckman Electroscan 30 Electroanalytical System.*

pH MODE

As a pH meter, the system provides a means for potentiometric measurement. Operation in this mode is illustrated in Figure 1. In solution, the glass and reference electrodes produce the net voltage (E_{in}) which is sensed at the summing point of the amplifier (AMP) and generates a current (i_f) in the feedback loop. This current gives a voltage drop ($i_f R_f$) which is opposite in polarity to E_{in}. As a result, the voltage around the summing loop is zero and i_f continues to flow at a constant rate proportional to E_{in}. The current through the recorder resistor (R_r) provides a voltage drop also proportional to E_{in} and read out on the potentiometric recorder.
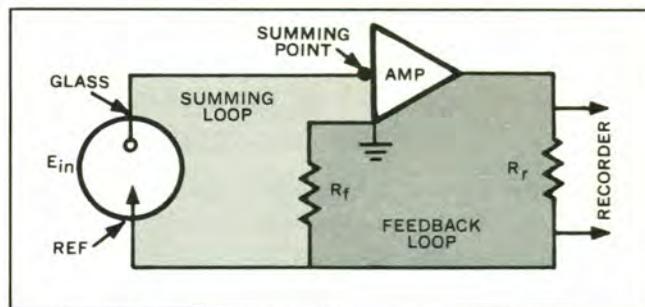
Figure 1. pH System.

GALVANOSTAT MODE

The Electroscan 30, used to create the controlled current for electrolysis, is shown in Figure 2. In this case, E_{in} is not generated by the electrodes but by a variable voltage source. The electrodes now are in the feedback loop. Again, E_{in} in the summing loop causes the amplifier system (AMP) to generate the current i_f in the feedback loop and the voltage drop, $i_f R_f$ which is equal and opposite to E_{in}. Since the cell is in the feedback loop, i_f also flows through it. Furthermore, as long as E_{in} and R_f are constant, i_f is constant, and a constant current passes through the cell. This electrolysis current can be changed in size and polarity by changing E_{in} or R_f. Finally, the current will not be affected by the cell resistance, R_c, provided that the product $i_f(R_c + R_f)$ does not exceed the power capabilities of the amplifier (30 volts). The

voltage at the surface of the working electrode is monitored by placing a reference electrode close to its surface and connecting both to the potentiometric recorder.
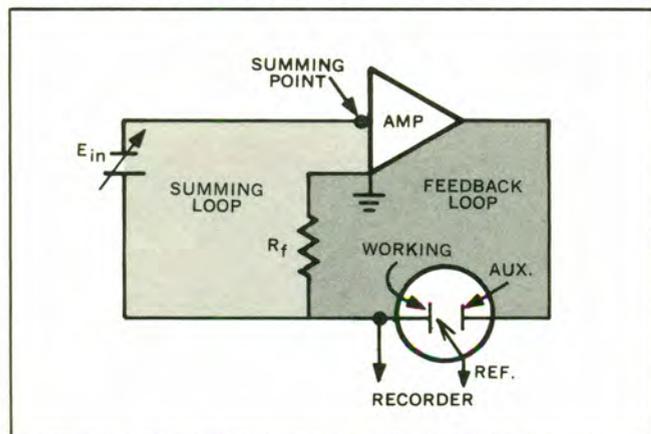
Figure 2. Galvanostat System.

POTENTIOSTAT MODE

In the potentiostat mode of operation, controlled potential techniques may be used. Three electrodes are employed as shown in Figure 3. The reference electrode is in the summing loop, the working electrode is located at the point of R_f in Figures 1 and 2, and the auxiliary electrode is in the feedback loop. For versatility, E_{in} is composed of three voltage sources. These are E_i, which is set at a fixed value; E_s, which can be varied linearly with

time; and E_R, the reference electrode voltage. An external voltage, E_{ex}, can also be applied. These voltages, E_i, E_s, E_R and E_{ex} are additive in the summing loop.
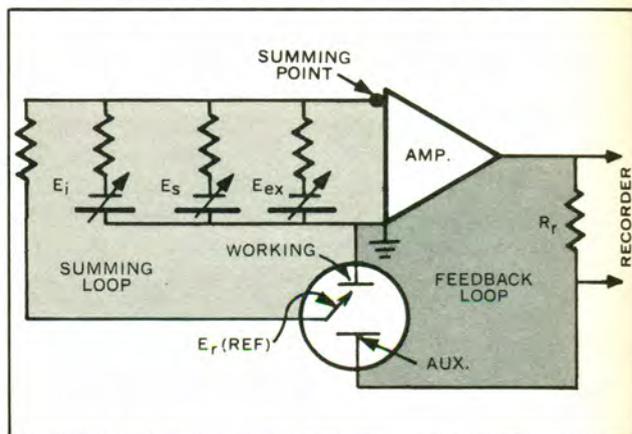
Figure 3. Potentiostat System.

In operation, the selected voltage, E_{in}, is sensed at the summing point of the amplifier. The amplifier then generates current, i_f, in the feedback loop through the cell by means of the working and auxiliary electrodes so the voltage at the working electrode surface is equal and opposite to E_{in}. Thus, the potential at the surface of the working electrode is selected by adjusting E_{in} and is controlled by the amplifier system independent of cell resistance provided the product $i_f R_c$ does not exceed the power capabilities of the amplifier (30 volts). The current i_f through the recorder resistor R_r, produces a voltage proportional to i_f which is read out on the recorder.

SECTION 2...ELECTROANALYTICAL PRINCIPLES

Electroanalytical techniques can be grouped into two main categories. These are voltammetry at zero current (potentiometry) and voltammetry at finite current (voltammetry). In potentiometry, potentials are measured while no significant amount of current is allowed to flow. In voltammetry, current is permitted to flow and electrolysis takes place in the electrochemical cell.

VOLTAMMETRY AT ZERO CURRENT (POTENTIOMETRY)

A fundamental consideration in potentiometry is the oxidation-reduction relationship existing between two species as described by:

$$Ox + ne^- \xrightleftharpoons[\text{OXIDATION}]{\text{REDUCTION}} Red \qquad (1)$$
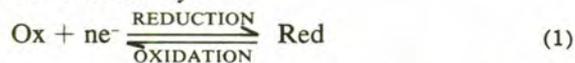
where Ox and Red are the oxidized and reduced forms, respectively, and n is the number of electrons, e^-, involved in the reaction. In the oxidation process, electrons are lost, and the species becomes more electropositive. In reduction, the reverse is true. For example, tripositive iron is reduced *to* the lower oxidation state when it gains an electron and is oxidized *from* the lower state by losing an electron:

$$Fe^{+3} + e^- \xrightleftharpoons[\text{OXIDATION}]{\text{REDUCTION}} Fe^{+2} \qquad (2)$$
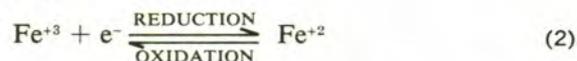
in which case n is one. In such systems, the oxidized and reduced forms constitute a *redox couple,* and, since they can undergo an electron transfer reaction, are said to be *electroactive.*

The Nernst Equation

When an electrode is brought into contact with a solution containing electroactive species, there is a tendency for the electrode to exchange electrons with the redox couples present. This tendency is a function of the electronic free energy of the electrode and the ions. It can be related thermodynamically to the solution composition. Thus, the electrical potential of an indicating electrode surface, relative to a reference voltage when no current is flowing, can be related to ionic activities by the *Nernst Equation:*

$$E = E° + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{Red}} \qquad (3)$$

where E is the electrical potential at the indicating electrode surface, $E°$ is the potential at the indicating electrode under standard conditions, R is the gas constant, T is absolute temperature, n is the number of electrons involved in the electrochemical reaction, F is Faraday's Constant, and a_{ox} and a_{Red} are the activities of the oxidized and reduced forms of the electroactive species present, respectively. Since most potentiometric measurements are made at 25°C and since most people are more familiar with logarithms to the base ten, a more convenient form of the Nernst Equation is:

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{a_{Ox}}{a_{Red}} \qquad (4)$$

Finally, the activity (a) of an ion in solution can be related to its concentration (C) as follows:

$$a = fC \qquad (5)$$

where f, the activity coefficient, is a measure of interaction between species in solution. As the concentration of the electroactive species approaches zero, f approaches unity.

The Indicating Electrode

As shown in Equation 3, the activity, and thereby the concentration, of a substance is determined from the potential at the indicating electrode surface. Several types of electrodes are used as indicating electrodes.

FIRST-CLASS ELECTRODE

A metal electrode in contact with a solution of its own ions will establish the following equilibrium:

$$M^{+n} + ne^- \rightleftarrows M^{\circ} \qquad (6)$$

The electrode is part of the redox couple and has an activity of unity. For example a silver electrode will give the reaction:

$$Ag^+ + e^- \rightleftarrows Ag^{\circ} \qquad (7)$$

The potential at the silver electrode surface is:

$$E = E^{\circ}_{Ag/Ag^+} + \frac{0.059}{1} \log a_{Ag^+} \qquad (8)$$

If E is plotted versus $\log a_{Ag^+}$ as in Figure 4, a straight line is obtained which has a slope of 0.059 volts and an intercept at $\log a_{Ag^+} = 0$ ($a_{Ag^+} = 1$) of E°_{Ag/Ag^+}.
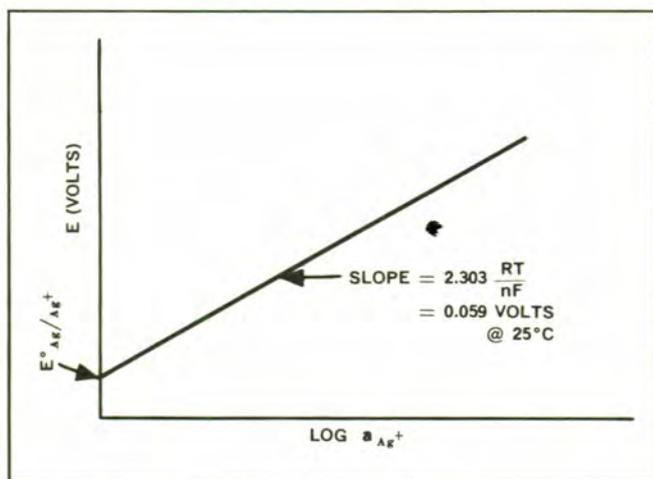
Figure 4. Plot of Potential Versus Log a_{Ag^+}.

SECOND-CLASS ELECTRODE

A metal electrode in contact with one of its slightly soluble or slightly dissociated salts and the anion of that salt is sensitive to the activity of the anion. For example, silver in contact with AgCl and Cl⁻ gives the electron transfer reaction:

$$Ag^+ + e^- \rightleftarrows Ag^{\circ} \qquad (9)$$

and the precipitation reaction:

$$Ag^+ + Cl^- \rightleftarrows AgCl \qquad (10)$$

The potential at the electrode surface is given by the equation:

$$E = E^{\circ}_{Ag/Ag^+} + \frac{0.059}{1} \log a_{Ag^+} \qquad (11)$$

However, since the silver ion activity is related to chloride ion activity through the relationship:

$$a_{Ag^+} = \frac{K_{sp}}{a_{Cl^-}} \qquad (12)$$

where K_{sp} is the solubility product constant of AgCl, the potential can be related to chloride ion activity by the equation:

$$E = E^{\circ}_{Ag/AgCl} + 0.059 \log \frac{1}{a_{Cl^-}} \qquad (13)$$

A plot of E versus $\log (1/a_{Cl^-})$, or $-\log a_{Cl^-}$, will give the straight-line relationship shown in Figure 5. Thus, second-class electrodes can be used to determine the activity of anions of slightly soluble salts such as:

Electrode	Anion
Ag/AgCl	Cl⁻
Ag/Ag₂S	S⁼ (and mercaptans)
Hg/Hg₂Cl₂	Cl⁻
Bi/BiF₃	F⁻
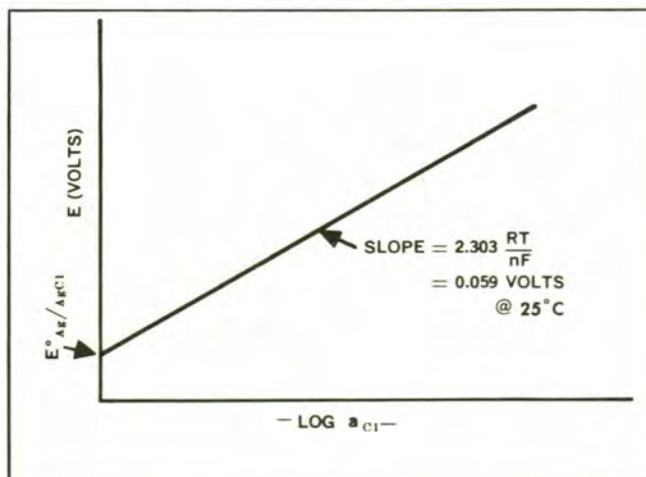
Figure 5. Plot of Potential Versus $-Log\ a_{Cl^-}$.

REDOX ELECTRODES

A relatively inert electrode in contact with a redox couple can give rise to an electron transfer reaction involving the couple. For example, a Pt electrode in a solution containing the Fe^{+3}, Fe^{+2} couple yields the reaction:

$$Fe^{+3} + e^- \rightleftarrows Fe^{+2} \qquad (14)$$

The potential at the electrode is given by the equation:

$$E = E^{\circ}_{Fe^{+3}/Fe^{+2}} + \frac{0.059}{1} \log \frac{a_{Fe^{+3}}}{a_{Fe^{+2}}} \qquad (15)$$

A plot of E versus log $a_{Fe^{+3}}/a_{Fe^{+2}}$ gives a straight line as shown in Figure 6.
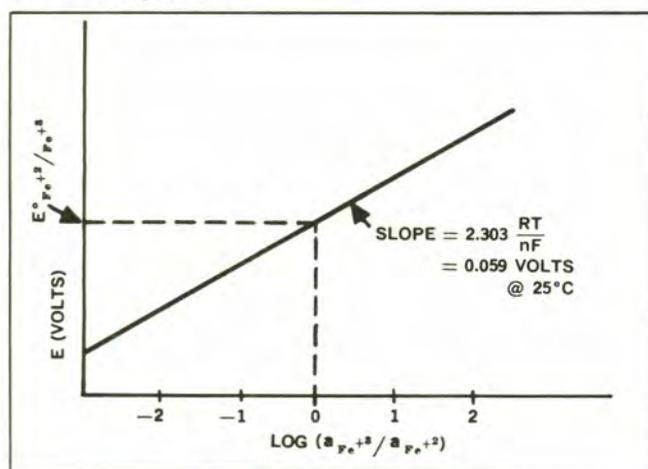
Figure 6. Plot of Potential Versus Log $a_{Fe^{+3}}/a_{Fe^{+2}}$.

MEMBRANE ELECTRODES

In the presence of certain ions, some membranes develop surface potentials which can be used to measure ionic activities. The best known of these are glasses which respond to hydronium ion (H_3O^+) activities and are used as pH electrodes. Others respond favorably to sodium, potassium, silver, and other ions and are used as pNa electrodes, pCation electrodes, etc.

For pH measurements, the potential of the electrode surface can be related to H_3O^+ activity by the following equations:

$$H_2O + H^+ = H_3O^+ \tag{16}$$

$$E = \epsilon + 0.059 \log \frac{a_{H_3O^+}}{a_{H_2O}} \tag{17}$$

In aqueous solutions, a_{H_2O} is a constant so the potential can be related to log $a_{H_3O^+}$. However, H_3O^+ activities usually are less than one, and, therefore, log $a_{H_3O^+}$ is usually negative. Accordingly, it is convenient to consider the negative of the log of $a_{H_3O^+}$ which is more commonly known as pH. Thus, Equation 17 becomes:

$$E = \epsilon' - 0.059 \, pH \tag{18}$$

where ϵ' is a constant similar to $E°$. Its value is a function of several factors including treatment of the membrane during fabrication. Because of this, ϵ' cannot be calculated reliably, and the relationship between E and log $a_{H_3O^+}$ must be determined experimentally as by calibration against a pH buffer standard.

The configuration of a pH measuring system is shown in Figure 7. R1 (Ag-AgCl reference electrode) and a constant pH solution are enclosed within the glass membrane to form a convenient probe. R2 can be one of several reference electrodes which is usually connected to the unknown pH solution through a liquid junction.
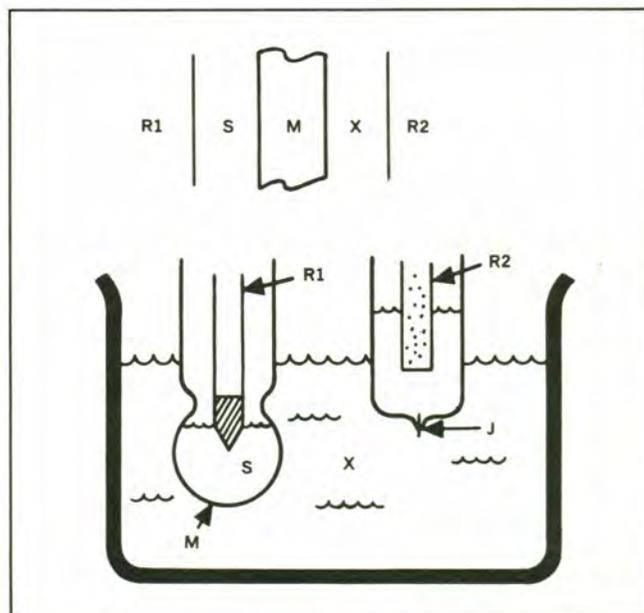
Figure 7. Schematic (a) and Physical Configuration (b) of pH Measuring System. R1 = Reference Electrode No. 1; R2 = Reference Electrode No. 2; S = Constant pH Solution; X = Unknown pH Solution; M = Glass Membrane; J = Liquid Junction.

The Reference Electrode

In order to measure the potential at an indicating electrode, the electrode is connected to one input of a voltmeter while the solution is, in some way, connected to the other, thus completing the measuring circuit. Although the solution connection could be made by a simple wire, this is not satisfactory because the solution-wire interface would develop uncertain potentials which would vary from one test to another. Therefore, the contact is made through a system which will produce an invariant potential regardless of time or solution composition. This is the function of a practical reference electrode which should have a repeatable and stable electrode surface which produces a known potential when in contact with an appropriate solution (filling solution); a filling solution containing proper ions to produce a stable potential when in contact with the reference electrode surface; and a restricted passage which allows the filling solution to make a good stable-potential contact with the sample solution without diluting or being diluted excessively by the sample solution. This is the liquid junction.

Among the many reference systems available, the most useful are the saturated calomel electrode (SCE) and the silver, silver chloride electrode (Ag,AgCl). Both are second-class electrodes.

In the SCE, the electrode surface is mercury coated with Hg_2Cl_2, while in the Ag,AgCl electrode, it is silver coated with AgCl-Ag. The filling solution in contact with the electrode is a saturated solution of KCl (SCE) or KCl + AgCl (Ag,AgCl). The restricted junction is often made through an asbestos fiber or ceramic plug.

These electrodes are actually secondary standards for providing reference potentials. The primary standard is the normal hydrogen electrode (NHE) which is a first-class electrode. By convention, the value for $E°$ in the NHE is 0.00 volts regardless of temperature. While the NHE is very reproducible, it is less convenient than the SCE and Ag, AgCl electrodes and, therefore, is used mainly to establish the potential of these secondary standards. Thus, at 25°C the potentials of the SCE and Ag, AgCl electrodes relative to the NHE are +0.244 volts and +0.200 volts, respectively.

VOLTAMMETRY AT FINITE CURRENT (VOLTAMMETRY)

Electrolysis simply refers to the process whereby solution components are converted from one oxidation state to another by means of a current flow at an electrode-solution surface:

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \qquad (19)$$

$$H_2O + e^- \rightarrow \tfrac{1}{2} H_2 + OH^- \qquad (20)$$
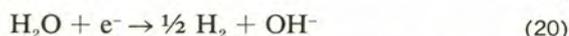
It should be noted that these reactions are different from the equilibrium systems involved in potentiometry (see Equation 1) in that an external driving force is applied.

Faraday's Law

The quantity of matter converted during electrolysis is related to the quantity of electricity passed through the solution. This relationship, discovered by Faraday, may be written:

$$Q = F \, Eq \qquad (21)$$

where Q is the quantity of electricity in coulombs, F is Faraday's Constant (96,490 coulombs/equivalent), and Eq is the number of equivalent weights of the electroactive species converted. The value of Q can be determined from the total current during electrolysis,

$$Q = \int_0^t i \, dt \qquad (22)$$

where i is the electrolysis current in amperes and t is time in seconds. If the electrolysis current is constant with time, Q is obtained simply by the equation,

$$Q = i \, (\Delta t) \qquad (23)$$

where Δt is the total time of electrolysis.

Cathode-Anode Considerations

In an electrolysis system the electrode which receives electrons from the external driving force and transmits these electrons to the reactant in solution, is denoted as the cathode. Its surface is where reduction occurs. The other electrode, the anode, receives electrons from solution and is the site of oxidation. Typical reactions at these electrodes are as follows:

$$\text{CATHODE} \quad Cu^{+2} + e^- \xrightarrow{\text{REDUCTION}} Cu^{+1} \qquad (24)$$

$$\text{ANODE} \quad 2\,H_2O \xrightarrow{\text{OXIDATION}} O_2 + 2H^+ + 2e^- \qquad (25)$$

Electron Transfer Process

When an electrode surface is in equilibrium with a solution, it exhibits a potential (E_e) which is thermodynamically related to the concentration of electroactive species present. The over-all electrode reaction:

$$Ox + ne \underset{\text{Oxidation }(i_a)}{\overset{\text{Reduction }(i_c)}{\rightleftharpoons}} Red \qquad (26)$$
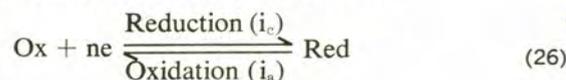
proceeds at a rate governed by (1) the rate at which electrons are transferred between the electrode and electroactive species, and (2) the rate of movement of electroactive material (mass transport) to the electrode surface. The over-all current (i) at an electrode is given by:

$$i = i_c + i_a \qquad (27)$$

where i_c, which is $(+)$, is the current due to the reduction reaction and i_a, which is $(-)$, is the current due to the oxidation reaction. At (E_{eq}) i_c equals i_a, and no net current flows.

When a voltage (E_{app}) is applied to the electrode which is different from E_{eq}, electrolysis takes place. As electrolysis proceeds, the composition of the electrode-solution interface approaches a new equilibrium condition. However, before a substance can undergo such a chemical transformation, an energy barrier must be overcome. Furthermore, the magnitude of this barrier determines the rate of transformation, and, therefore, the amount of current during an electrochemical reaction. The driving force necessary to overcome the energy barrier is the applied voltage. In this case, the standard rate constant (k_s) for the electron transfer process is composed of a cathodic rate constant (k_c) and an anodic rate constant (k_a):

$$Ce^{+4} + e^- \underset{\text{Anodic }(k_a)}{\overset{\overset{\textstyle k_s}{\text{Cathodic }(k_c)}}{\rightleftharpoons}} Ce^{+3} \qquad (28)$$
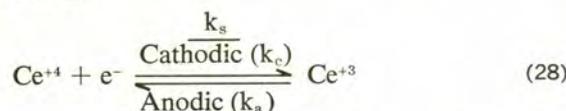
If the mass transport rate is sufficiently fast, i will be independent of time and limited by the electron transfer rate and:

$$i_c = nFC°_{ox} \, k_c \qquad (29)$$

$$i_a = nFC°_{Red} \, k_a \qquad (30)$$

where $C°_{ox}$ and $C°_{Red}$ are the concentrations of the oxidized and reduced species at the electrode surface. These rate constants are in turn given by:

$$k_c = k_c° \, \exp\,[-\alpha nF\,(E_{app})/RT] \qquad (31)$$

$$k_a = k_a° \, \exp\,[(1-\alpha)nF(E_{app})/RT] \qquad (32)$$

where $k_c°$ and $k_a°$ are the formal rate constants at $E_{app} = 0$ and α is that fraction of E_{app} which enhances

the rate of the cathodic reaction over that of the anodic reaction. Also:

$$k_c^\circ / k_a^\circ = \exp(nF\, E_{eq}^\circ / RT) \tag{33}$$

where E_{eq}° is the standard equilibrium potential under standard conditions (i.e., $C_{Ox} = C_{Red}$). Also, when:

$$E_{app} = E_{eq}^\circ \tag{34}$$

and $k_c^\circ / k_a^\circ = 1$, $\tag{35}$

$$k_c^\circ = k_a^\circ = k_s \tag{36}$$

For very fast electron transfer rates, k_s is large, and the electrode process is said to be reversible. On the other hand, very small values of k_s are indicative of an irreversible process.
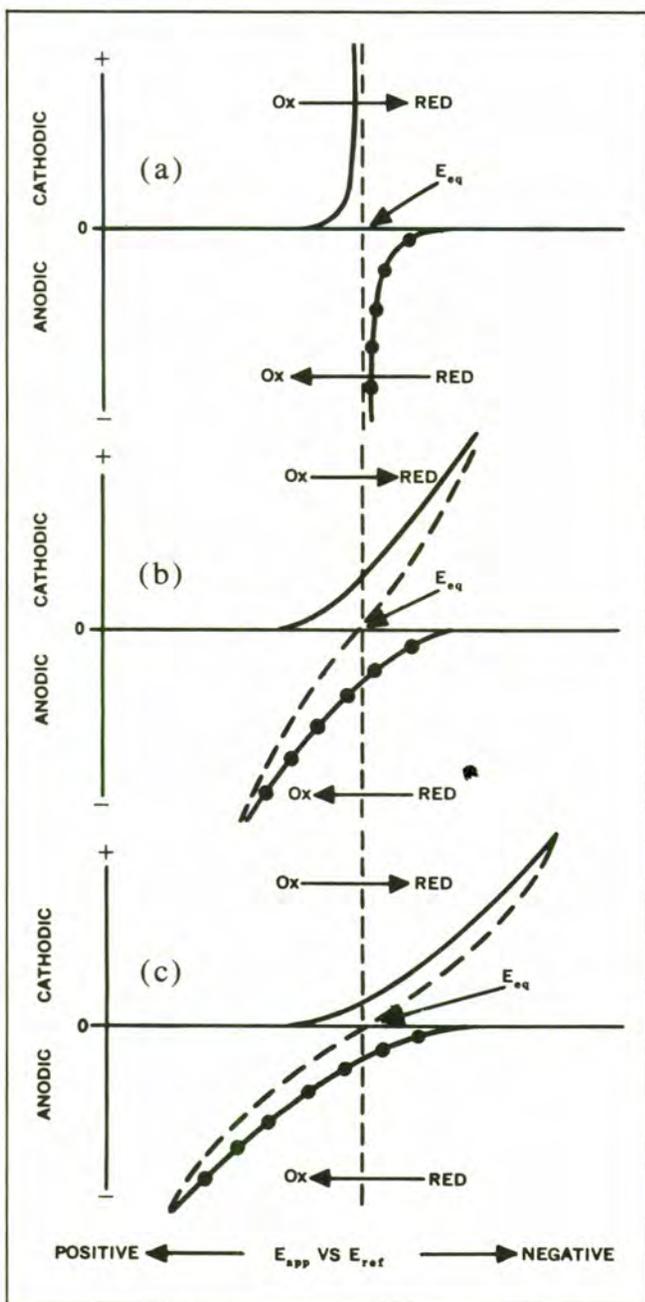
Figure 8. Idealized i-E Curve where (a) k_s is Large, (b) k_s is Small, and (c) k_s is Very Small.

IDEALIZED CURRENT-VOLTAGE CURVES

When a voltage is applied to a pair of inert electrodes, specific relationships exist between current and voltage which depend upon the electroactive species present in solution. Idealized curves for these are given in Figure 8. As shown, voltages which polarize the electrode more negatively (better electron donor) are plotted with increased values to the right, while those which polarize the electrode more positively increase to the left. The current which flows during reduction (positive current) is plotted upward while the oxidation current (negative current) is plotted downward.

When the electroactive species is present only in the oxidized form and the applied voltage is sufficiently negative, reduction occurs at the electrode surface and cathodic current flows. This corresponds to the curve in Figure 8a.

As voltage becomes more negative, more current flows. This increase in positive current is very steep if k_s is very large. If only the reduced form is present, the reverse current will flow as E_{app} is scanned from negative to positive. If both forms are present, the current will change very rapidly from positive to negative, or vice versa, as E_{app} is scanned through E_{eq}. Similar relationships exist when current is applied and voltage is measured. If the electron transfer mechanism is slow (i.e., small k_s), the slope of the i-E curve is not as steep and becomes even shallower for very small values of k_s. These effects are shown in Figures 8b and 8c.

Mass Transport Mechanisms

During electrolysis, the decrease of reactant concentration at the electrode surface affects both electrode potential and electrolysis current. Therefore, the mass transport rate (rate at which reactants move from the bulk of the solution to the electrode surface) is an important factor in all electrochemical reactions involving electrolysis. There are three basic mechanisms by which mass transfer is achieved; migration, diffusion, and convection.

Migration

Migration involves ionic movement due to electrical gradients whereby ions are attracted by the electrode of opposite charge. This is illustrated in Figure 9 for a ferric chloride solution.
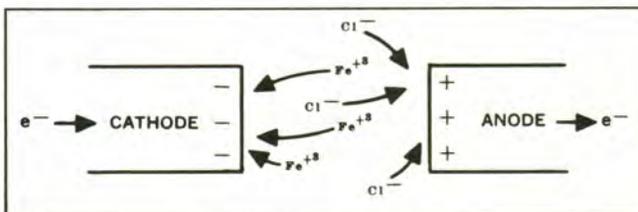
Figure 9. Migration of Ions in Solution.

9

It is usually desirable to eliminate migration in volt-ammetry. This can be done by adding a *supporting electrolyte* which is (a) electrochemically more inert and (b) more abundant than the electroactive species so that it accounts for nearly all migration. For example, if KCl at 100 times greater concentration were added to the $FeCl_3$ solution, the Fe^{+3} migration would be reduced to about 1% of its previous value.

Diffusion

Diffusion is the movement caused by concentration gradients. During electrolysis, the concentrations of some species are decreased at the electrode surface while others are increased. Concentration gradients are created which cause ions and molecules to diffuse. The thickness of the diffusion layer (δ) increases with time and never reaches a limiting value even when the concentration of the diffusing species at the electrode surface becomes zero. When some other means of mass transfer is operative, such as reproducible stirring, (δ) reaches a steady limiting value. Compared to mechanical stirring, diffusion is relatively slow.

Each ion or molecule has a characteristic diffusion rate which depends upon its own properties as well as those of the solvent. The rate is practically independent of other electrolytes surrounding it. This rate is expressed as the diffusion coefficient (D) in cm^2/sec. The limiting current, i_{lim}, which can flow during electrolysis is related to the diffusion coefficient in the equation:

$$i_{lim} = \frac{nFDC_bA}{\delta} \qquad (37)$$

where C_b is the concentration of the diffusing species in the bulk of the solution and A is the area of the electrode surface.

Convection

Convection is the movement caused by mechanical or thermal agitation. Mechanical stirring increases the mass transport rate and reduces and stabilizes the diffusion layer. This results in an increase in limiting current. Therefore, the rate of stirring must be controlled if a constant current is to be obtained. Control may be achieved either at zero rate (quiescent solution) or at some finite rate. However, quiet solutions are difficult to maintain over periods longer than 100-200 seconds because of thermal convections.

EFFECT OF MASS TRANSPORT ON CURRENT-VOLTAGE CURVES

The i-E curves in Figure 8 apply to solutions in which the mass transport rate (MTR) approaches infinity, but this is not achieved in practice. Accordingly, the curves in Figure 10 are more realistic. Examples of cathodic current reactions are given here. Curves for anodic current reactions are similar.
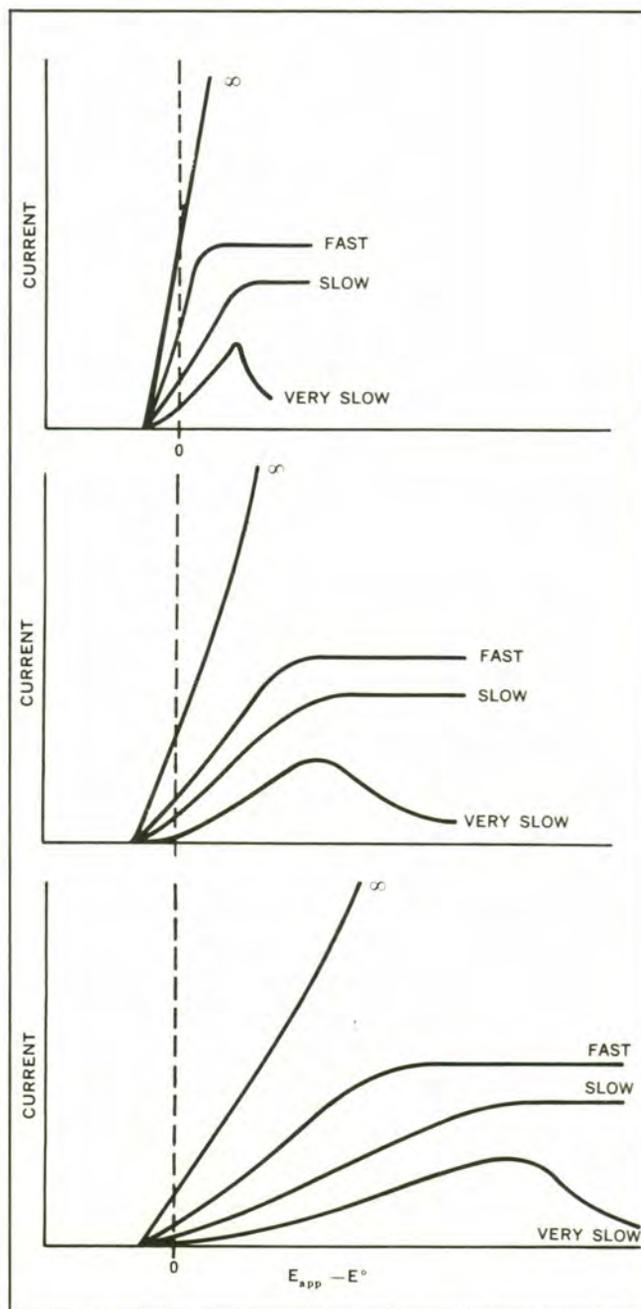
Figure 10. Idealized i-E Curves Modified by MTR with (a) Fast, (b) Slow, and (c) Very Slow Electron Transfer Rates.

As shown in these curves, current increases as the applied voltage becomes more negative. In the early stages, the MTR is sufficient to replace those species lost at the electrode, and the electrochemical kinetics, or electron transfer rate (ETR), limits the current flow. However, as E_{app} becomes more negative, k_c increases and eventually the ETR exceeds the MTR. At this point current no longer increases with E_{app} and is now limited by the MTR. Thus, a fast MTR gives a high limiting current and a slow MTR gives a low limiting current.

If the MTR is very slow, as in a quiet solution where diffusion is the sole factor, a peaked curve usually

results. The current rises abruptly at first as the electro-active species at or near the surface are electrolyzed, then decays because the MTR is not sufficient to support the current flow.

As seen in the progression given in Figures 10a, 10b, and 10c, the ETR also affects the slope of the curves. However, as long as sufficient potential is applied, the same limiting current is reached in each case for the same MTR.

Significance of Current-Voltage Curves

HALF-WAVE POTENTIAL

The potential at which the current is half its limiting value is known as the half-wave potential ($E_{1/2}$), one of the most useful properties of an electroactive substance. When fast electron transfer rates are involved, $E_{1/2}$ is equal to $E°$ of the Nernst Equation. For slow rates, more voltage than predicted by the Nernst Equation is required to reach the $E_{1/2}$ point. These differing conditions are shown in Figures 11a and 11b, respectively. For the second case, the additional voltage required is the over-voltage (η).
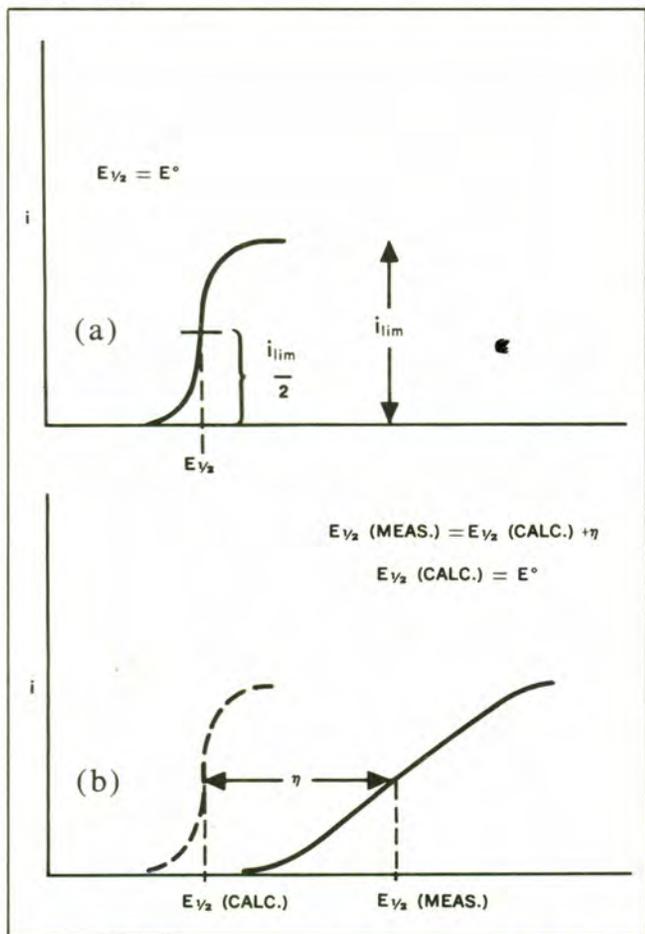
Figure 11. Half-Wave Potential Curves for (a) Fast ETR and (b) Slow ETR.

OTHER FEATURES OF CURRENT-VOLTAGE CURVES

In Equation 37 it is seen that the limiting current, i_{lim}, actually depends upon several factors including n, the number of electrons involved in the reaction, and C_b, the concentration of the electroactive species. These are illustrated in Figure 12.
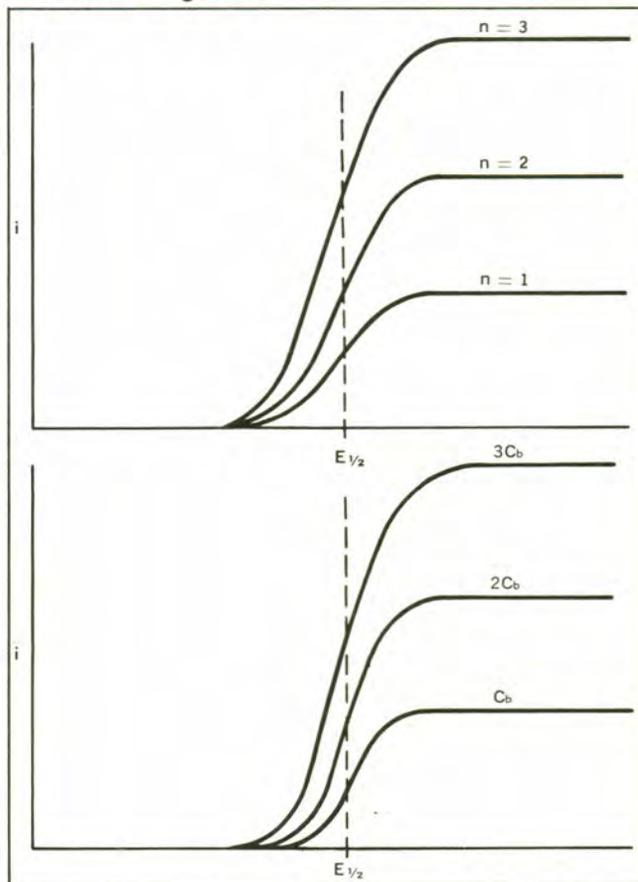
Figure 12. Effect of (a) n and (b) C_b on the Limiting Current (other factors being constant).

MULTICOMPONENT SYSTEM

When more than one electroactive species is present, each one is electrolyzed at the E_{app} sufficient to overcome its particular energy barrier. Accordingly, these components can be electrolyzed sequentially if their $E_{1/2}$ values
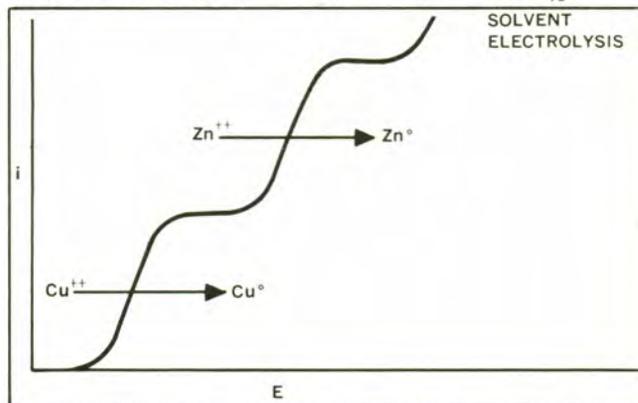
Figure 13. Current-Voltage Curves for a Multicomponent System.

are significantly different and they are more electroactive than the solvent. Usually, about 0.2 V is necessary for good resolution. These conditions are illustrated in Figure 13.

Solvent Electrode Limitations

Both solvent condition and electrode material affect the electrochemical kinetics, and, therefore, $E_{1/2}$ for a given electrolysis depends upon experimental conditions. Furthermore, each solvent-electrode system limits the useful potential range since the solvent itself will eventually be electrolyzed. In Figure 14 useful ranges for various solvent-electrode combinations are indicated.

SOLVENT	ELECTRODE		
WATER	Mercury	Oxidation of mercury ≣ -Ag——Cu——Pb—Cd——Zn-Ni—Co-Cr Fe -Mn—Al-Ba-Rb-Na-Sr-K-Ca-Li-≣	Reduction of water
	Platinum	Oxidation of water ———— ↔ –Hg-Ag——Cu——Pb—Tl—≣	Reduction of water
		500 mV	
LIQUID AMMONIA (−36°C)	Mercury	----Tl———Cu———————Cs-Rb-K-Na——Li----	
DIMETHYL FORMAMIDE	Mercury	Oxidation of mercury ≣—Cu————Ni-Zn-Co-Rb Ba - K Na -Sr-Ca-Li———	Reduction of indifferent electrolyte (R_4N^+)
FORMAMIDE ACETAMIDE	Mercury	Oxidation of mercury ≣—Tl-Pb————Zn————K———---------	Reduction of indifferent electrolyte
ETHYLENE DIAMINE	Mercury	Oxidation of mercury ≣———Tl—Cd———Pb—Zn-Ca Sr Ba Mg -Ag-----difference electrolyte or solvent?	Reduction of in-
ACETO-NITRILE	Mercury	Oxidation of Mercury ≣—Ag——Ni-Cu-Cd-Co-Zn——Fe-Cr-Mn——Al-Be-Ba-Mg Sr Na Ca Rb K -Li--------	Reduction of indifferent electrolyte
	Platinum	Oxidation of acetonitrile ≣— ↔ ———Hg———Ag——Cu-Cd———Zn————————Li-------	Reduction of indifferent electrolyte
		2 v	
FUSED EUTECTIC LiNO₃-NaNO₃-KNO₃ (160°C)	Mercury	Oxidation of mercury ≣———Ni-Pb-Cd—Zn——≣	Reduction of Nitrates
FUSED EUTECTIC LiCl-KCl (450°C)	Platinum	Oxidation of platinum ≣———Bi-Hg-In-Ga-Sn-Co-Pb-Cu—Cd—Tl-Zn—Cr-Al———≣	Reduction of solvent (deposition of K-Li)
	Graphite	Oxidation of chlorides ≣————Pt————————Pb—————≣	Reduction of solvent
		1 volt	

Figure 14. Ranges for Solvent-Electrode Combinations.[1]

[1]G. Charlot, J. Badoz-Lambling, B. Tremillon, *Electrochemical Reactions*. New York: Elsevier, 1962, p. 354.

SECTION 3...ELECTROANALYTICAL TECHNIQUES

POTENTIOMETRY

Definition

Potentiometry involves measurement of the electrical potential or the electromotive force (EMF) at an electrode surface (indicating electrode) relative to a reference voltage (reference electrode). In *zero current* potentiometry, no net electrochemical reaction occurs at the indicating electrode, and the measurement is independent of mass transport. In *constant current* potentiometry, a small current flows through the indicating electrode. In a stirred solution, the current is sufficiently small that a stable potential is achieved due to diffusion of the electroactive species present.

Important applications of potentiometry include direct determination of ionic activity (direct potentiometry, e.g., pH, pNa, pCl), and end point detection for volumetric titrations (potentiometric titrations).

Instrumentation

For pH and other potentiometric measurements requiring a high-impedance amplifier, the pH mode of the Electroscan 30 Electroanalytical System is used. For this, the indicating electrode is connected to the glass electrode terminal as shown in Figure 15a. Low-impedance electrodes can also be used this way or alternately with the electrolysis display mode. In this case, the indicating electrode is connected to the working electrode terminal. Either zero current or a constant positive or negative current is applied to it. If current is applied, an auxiliary electrode must also be added as shown in Figure 15b.
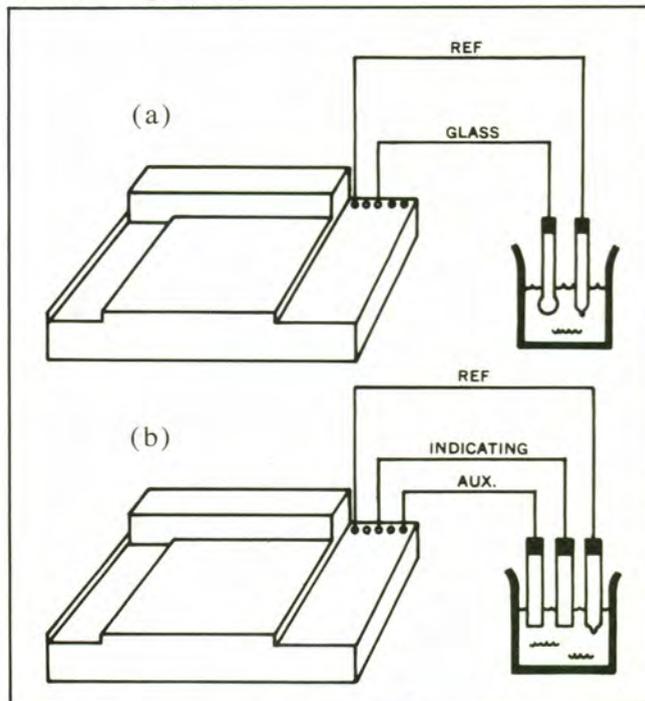
Figure 15. Instrumental Configuration for (a) High-Impedance and (b) Constant Current Potentiometric Measurements.

13

Principle

The principles of this technique are covered under voltammetry. (See VOLTAMMETRY AT ZERO CURRENT, page 5).

Applications

Direct potentiometry has been applied most successfully to pH and chloride ion measurements, although it has been used for direct measurement of Na^+, $S^=$, Ag^+, and several other ions. It has also been used for redox potential measurements. Unfortunately, there are only a few ion-specific membrane and second-class electrodes available. Redox electrodes lack specificity for general analytical use, and most first-class electrodes (e.g., Pb^{+2}/Pb°) also lack specificity. However, use of these electrodes as end point indicators broadens their usefulness considerably since the titrant supplies the specificity required.

Advantages and Limitations

Potentiometry is a continuous measurement offering simplicity in both technique and instrumentation. It provides speed with most indicating electrodes reaching equilibrium in 10 seconds. With use of glass electrodes for pH and second-class electrodes, such as Ag, AgCl for Cl^- and Ag, Ag_2S for sulfides and mercaptans, the technique has good selectivity. Lastly, potentiometry has a dynamic range where reliable measurements can be made over several decades of concentration.

On the other hand, accuracy is limited by two major factors in direct potentiometric work: (1) variations in liquid junction potential of the reference electrode, which can give errors of 2-3% and (2) uncertainties in activity coefficients which are needed to convert activities (measured) into concentrations (desired). These problems are eliminated when potentiometry is used as an end point detector in a volumetric titration. Additionally, interferences are also a limitation because specific indicating electrodes are not available for all types of ions.

POLAROGRAPHY

Definition

Polarography is a controlled potential technique in which the electrolysis of an analyte occurs at a dropping mercury electrode (DME), where the potential of the DME is constant or varied linearly with time. Convective diffusion of the analyte is the only means of mass transport. The electrolysis current is displayed against the controlled potential of the DME.

Instrumentation

The Electroscan 30 Electroanalytical System, and an appropriate electrolysis cell, can be used for controlled potential polarographic analysis. With the arrangement shown in Figure 16, the potentiostat controls the DME potential versus the potential of the reference electrode. This potential can then be held constant or scanned linearly with time.
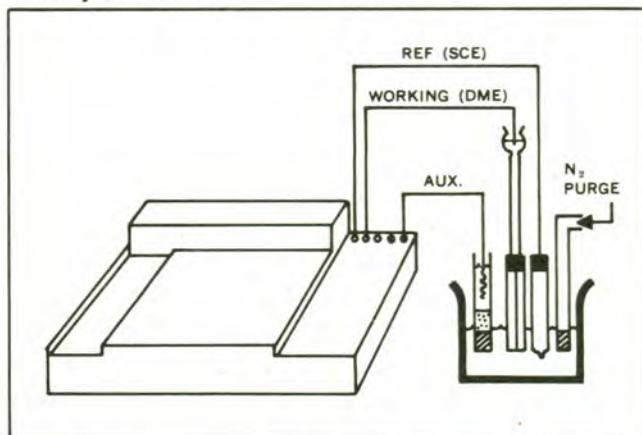
Figure 16. Instrumental Configuration for Polarography.

The DME consists of a length of marine barometer tubing with a fine capillary and a head of mercury above it. The mercury head is usually adjusted to give a drop time of 2-5 seconds. The auxiliary electrode is isolated from the test solution by a sintered glass disk and an agar plug in order to reduce contamination of the test solution by its products. The reference electrode is usually a saturated calomel electrode. The test solution must be purged with high-purity nitrogen to remove oxygen interference.

Principle

TYPICAL CURRENT-POTENTIAL CURVE

A typical (i-E) curve or polarogram is shown in Figure 17. Curve (a) is that of a 1F HCl solution while Curve (b) is that of $1 \times 10^{-3}F$ Cd^{++} in 1F HCl.
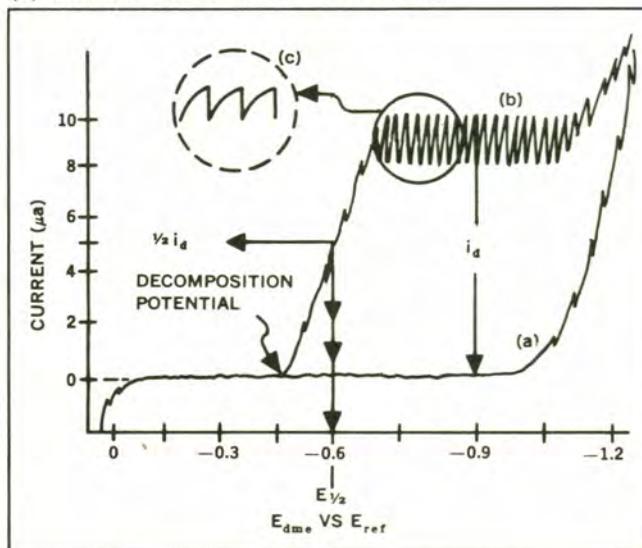
Figure 17. Polarogram of Cd^{++} in 1F HCl.

In this example, the potential at the DME (E_{dme}) is scanned in the negative direction. At first, the current in Curve (a) is zero, then rises gradually due to trace impurities and charging of the double-layer capacitance at the mercury-solution interface. This current is called the residial current (i_r). Finally, the decomposition potential of hydrogen is reached and the current rises sharply. In Curve (b), the current rises sharply from that produced by the solvent when the decomposition potential of Cd^{++} is reached:

$$Cd^{++} + Hg + 2e^- \; \xrightleftharpoons{\hspace{2cm}} \; Cd(Hg) \qquad (38)$$

As the current starts to rise, it is controlled by diffusion of Cd^{++} (or by the kinetics of the electron transfer reaction for irreversible cases) and eventually becomes limited by the net rate at which Cd^{++} diffuses to the electrode. This limitation produces a current plateau which continues until a potential sufficient to electrolyze another electroactive species is reached. The net current produced by the diffusion of the electrolyzed species in the plateau region is called the diffusion current (i_d). The total current in the plateau region, including i_r and i_d, is called the limiting current (i_{lim}).

The oscillations seen in these curves are due to the growth and fall of the mercury drops. As shown in the Inset (c), the current increases as the drop grows, and then drops sharply when the mercury drop detaches itself and falls.

The value of i_d during the drop life is given by the Ilkovic Equation:

$$(i_d)_{max} = 708 \; nm^{2/3} \; t^{1/6} \; D^{1/2} \; C_b \text{ at } 25° \qquad (39)$$

where $(i_d)_{max}$ equals the diffusion current (μa) at t, n equals the number of electrons in the electron transfer reaction, m equals the average Hg flow rate (mg/sec.), t equals the drop life (sec.), D equals the diffusion coefficient of the electroactive species (cm^2/sec), and C_b equals the concentration (mM) of the analyte in the bulk of the solution.

When a fast recording system is used (i.e., <1 second full scale response), the peaks of the oscillations equal $(i_d)_{max}$. When the recording system is damped, the average diffusion current $(i_d)_{ave}$ is determined from the average of the recorded oscillations. $(i_d)_{max}$ can be calculated from the relationship:

$$(i_d)_{max} = 7/6 \; (i_d)_{ave} \qquad (40)$$

CURRENT-POTENTIAL RELATIONSHIP

The potential where i is $1/2$ of i_d is called the half-wave potential. If the electron transfer reaction is fast (i.e., reversible), then at 25°C:

$$E_{dme} = E_{1/2} - \frac{0.059}{n} \log \frac{i - (i_d)_a}{(i_d)_c - i} \qquad (41)$$

and

$$E_{1/2} = E^{°'} - \frac{0.059}{n} \log \frac{D_{Ox}}{D_{Red}} \qquad (42)$$

where E_{dme} equals the potential of the DME, $E^{°'}$ equals the formal potential of the half reaction, n equals the number of electrons in the electron transfer reaction, i equals the electrolysis current, $(i_d)_a$ equals the anodic diffusion current, $(i_d)_c$ equals the cathodic diffusion current, D_{Ox} equals the diffusion coefficient of the oxidized form, and D_{Red} equals the diffusion coefficient of the reduced form. Since D_{Ox}/D_{Red} is usually close to 1, $E_{1/2}$ equals $E^{°'}$.

If the electron transfer reaction is very slow (i.e., irreversible), then for a cathodic wave:

$$E_{dme} = E_{1/2} - \frac{0.054}{\alpha n_a} \log \frac{i}{i_d - i} \qquad (43)$$

$$E_{1/2} = \frac{0.059}{\alpha n_a} \log (1.349 \; k_c \; t^{1/2}/D_{Ox}^{1/2}) \qquad (44)$$

where α equals the transfer coefficient and k_c equals the rate constant for the cathodic reaction.

From the Equation 44, it is obvious that for irreversible systems, $E_{1/2}$ is strongly influenced by the kinetic factors k_c and α.

MAXIMA

Polarograms often exhibit current maximum as shown in Figure 18.
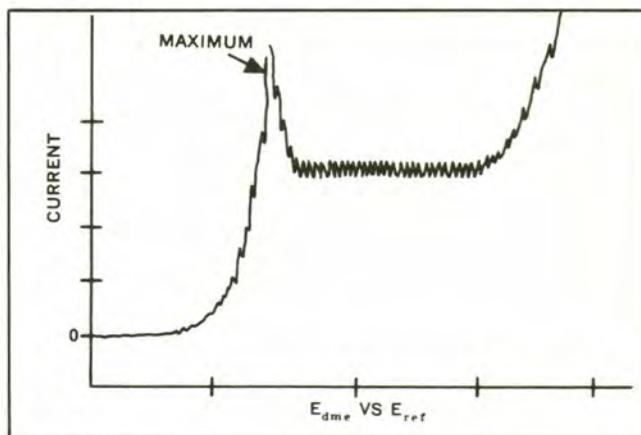
Figure 18. Polarogram Exhibiting Maximum.

These are due to the streaming of solutions past the mercury surface at certain potentials. These maximum can often obscure the wave of interest. Often, they can be eliminated by adding a small amount ($\approx 0.003\%$) of surface-active material, such as gelatin.

Applications

QUALITATIVE ANALYSIS

Extensive tables (see PRIMARY SOURCES OF INFORMATION, page 1) exist for the $E_{1/2}$ of electroactive substances in a variety of solvent-supporting electrolyte media. Thus, an $E_{1/2}$ value from the polarogram of an unknown sample can be indicative of a relatively small number of possible substances. Polarographing the

unknown in various media may then provide sufficient differentiation for final identification. This is possible, because the media often have different effects upon the kinetics of the electron transfer reaction.

The reason that various media change the relative $E_{1/2}$ values of certain substances is that they affect the thermodynamics or kinetics of the electron transfer reaction (e.g., complex formation, overvoltage, and reversibility). For example, $E_{1/2}$ for both Cu^{++} and Bi^{++} is -0.01 volts versus SCE in $1F$ HNO_3. However, in $0.1F$ potassium biphthalate, their $E_{1/2}$ values are -0.10 volts and -0.23 volts versus SCE, respectively.

DIRECT QUANTITATIVE ANALYSIS

Quantitative work depends upon the relationship between the i_d and concentration.

Sensitivity

Quantitative polarography has been most successfully applied in the 10^{-2} to 10^{-5} formal region. At higher concentrations, solubility factors at the surface of the mercury drop often give spurious results. At concentrations lower than $10^{-4}F$, the residual current is often as large as the diffusion current. Thus, the problem of trying to measure a small change in a large signal results, which severely limits precision.

Selectivity

The current waves or steps occur in the order of the $E_{1/2}$ values of the species in solution. The first species to be electrolyzed can be determined with the greatest reliability. The selectivity depends greatly upon the solvent used as pointed out under Qualitative Analysis. When analyzing a multicomponent system, species with $E_{1/2}$ values differing by 150 mv or greater can usually be resolved.

Accuracy

By rearranging Equation 39, we can see that:

$$C_b = (i_d)_{max}/708n\ D^{1/2}\ m^{2/3}\ t^{1/6} \qquad (45)$$

For a given substance in a given medium, the diffusion current constant $708n\ D^{1/2}$ (sometimes tabulated as I), is constant, and the capillary constants ($m^{2/3}\ t^{1/6}$) can be measured. Once these constants have been determined, this equation can be used to estimate C_b directly from a measurement of $(i_d)_{max}$ without the need of calibration standards. In practice, this procedure gives results which have an error in the order of $\pm5\%$.

For additional accuracy, standards can be polarographed to determine the proportionality constant k in:

$$C_b = k\ (i_d)_{max} \qquad (46)$$

This procedure can yield accuracies in the order of $1-2\%$.

QUANTITATIVE ANALYSIS BY TITRATION (AMPEROMETRIC TITRATION)

A polarized DME can function as an indicator electrode in a titration. The potential at the DME is set so as to electrolyze the reactant, titrant, and/or products of the titration. The potential is selected so as to give the sharpest end point indication and the electrolysis current is plotted against titrant volume.

Sensitivity

Amperometric titrations have about the same sensitivity limits as direct polarography.

Selectivity

The selectivity of the titrant combined with the ability to choose the electrolysis potential often makes amperometric titrations more selective than potentiometric titrations.

Accuracy

Like most titration techniques, the accuracy of the amperometric technique is often better than 1%.

KINETIC STUDIES

The kinetic parameters α and k can be evaluated from a polarogram using Equations 43 and 44.

A plot of $\log (i/i_d - i)$ versus E_{dme} gives a straight line with a slope equal to $0.054/\alpha n_a$, from which α can be calculated. Once α is known, the rate constant k_c can then be calculated from Equation 44.

Advantages and Limitations

Polarography shares the same advantages possessed by all voltammetric techniques in that the recorded traces contain qualitative, quantitative, and kinetic information. It can also be applied to an extremely broad range of inorganic cations, anions, and organic functional groups.

The DME offers three additional advantages over other voltammetric techniques. These are controlled and repeatable stirring caused by the growth and fall of the mercury drop; new, uncontaminated electrode surface with each new drop; and large hydrogen overvoltage which extends its range of application in the negative region.

The disadvantages of the technique include the occasional fouling of the capillary tip as well as the time requirement for running a good polarogram, which takes several minutes. The presence of maxima is another limiting factor. Furthermore, polarography is limited to potentials more negative than 0.5 volts versus SCE due to the oxidation of mercury. With anions, which form slightly soluble or ionized mercury salts, this potential is limited further.

SOLID ELECTRODE VOLTAMMETRY

Definition

Solid electrode voltammetry is a technique in which the electrolysis of an analyte occurs at the surface of a fixed-area electrode in a stirred solution. The surface potential is either constant or varied linearly with time. Diffusion and convection due to constant rapid stirring are the means of mass transport. Electrolysis current is displayed against the controlled potential. Typical working electrodes used are platinum, gold, boron carbide, pyrolytic graphite, and carbon paste. To a large extent, the applications of this technique are the same as those of polarography.

Instrumentation

The instrumental configuration for this technique is shown in Figure 19. The potentiostat controls the working electrode potential versus the potential of the reference electrode. This potential can then be held constant or scanned linearly with time. As in polarography, the working electrode is moved relative to the solution. This is most often accomplished by mounting the electrode in a chuck, which is rotated at a constant rate by a synchronous motor. The essential features of such an electrode arrangement are shown in Figure 20.
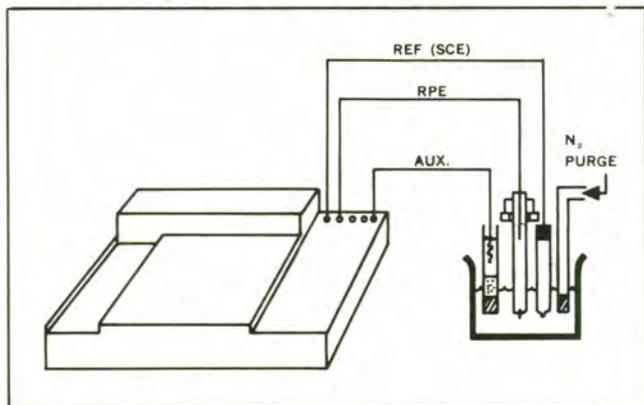
Figure 19. Instrumental Configuration for Solid Electrode Voltammetry.
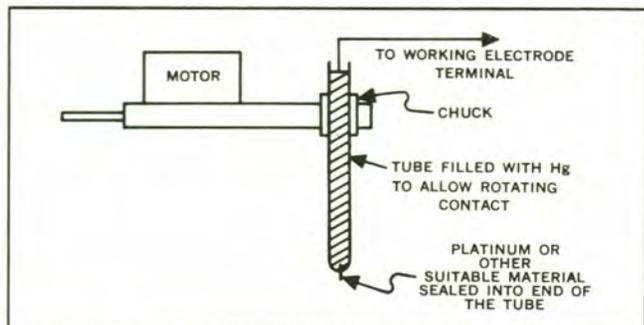
Figure 20. Rotating Electrode Assembly.

Principle

TYPICAL VOLTAMMOGRAM

A typical voltammogram is shown in Figure 21.
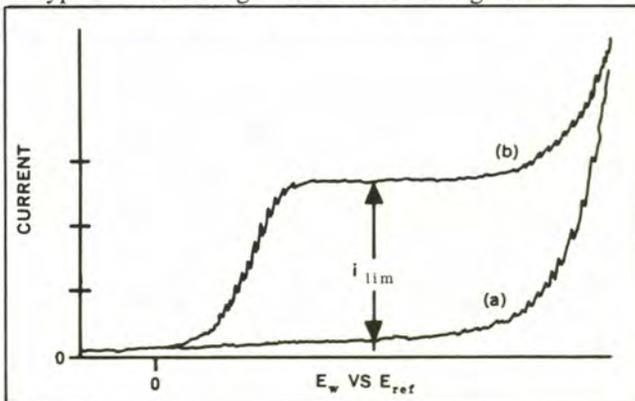
Figure 21. Typical Voltammogram.

As in the case of polarography, (a) is the i-E curve for the solvent-supporting electrolyte system and (b) is the curve for the same system with an electroactive analyte added.

INTERPRETATION OF LIMITING CURRENT

The over-all interpretation of these curves is the same as that for the polarographic curves. However, oscillations in the recorded curves are rather erratic and are caused by turbulence at the rotating electrode surface.

In solid electrode voltammetry, the electrolysis current is due to both diffusion and convection. The current in the plateau region is called the limiting current (i_{lim}) and it is estimated from the average of the current oscillations. The equation for this current is:

$$i_{lim} = \frac{nFADC_b}{\delta} \tag{47}$$

which was defined earlier (Equation 37).

Since the stirring rate affects the thickness of the diffusion layer (δ), Equation 47 can be rewritten as follows:

$$i_{lim} = M_{rot} nFADC_b \tag{48}$$

where M_{rot} is the mass transport coefficient for the rotating electrode. Unfortunately, M_{rot} is a function of many factors, including electrode and cell design. Consequently, it cannot be rigorously defined except in certain special cases. However, when a certain electrode and cell design is consistently used, M_{rot} is a repeatable proportionality constant. Equation 48 can be used for quantitative analysis by experimentally determining M_{rot} with standard solutions.

Applications

In general, the discussion of qualitative and quantitative applications presented for polarography are applicable to solid electrode voltammetry. This technique has been

extensively used for amperometric titrations. The study of kinetic factors is similarly applicable.

Advantages and Limitations

There are two basic reasons for using a rotated, fixed-surface electrode in preference to a DME. These are increased signal and greater usable potential range. The increase in signal results from the enhanced mass transport caused by rapid stirring. At typical stirring rates of 600 rpm, there is about a five-fold increase of signal-to-background ratio, as compared to polarography.

The potential range in volts (versus SCE) of platinum in aqueous media at various pH values is illustrated in Figure 22.

pH	Positive	Negative
1	+1.1	−0.3
7	+0.8	−0.6
13	+0.4	−1.0

Figure 22. Table of Voltage Ranges of Platinum at Various pH Values.

The potential range of gold varies from that of platinum to as much as 0.5 volt more positive or negative, depending upon the supporting electrolyte used. The presence of chloride ions severely decreases the potential range of both platinum and gold electrodes. Boron carbide (B_4C) has a potential range of +0.9 to −1.3 volts versus SCE in 1M H_2SO_4 and slightly less in other media. The various graphite electrodes (e.g., pyrolytic, wax impregnated, and mineral oil paste electrodes) have a potential range similar to gold, and can be used in strong chloride media.

There are two fundamental limitations of fixed-surface electrodes compared to the DME. These are less repeatable mass transport, and surface contamination. Although the mass transport due to rotation is repeatable, it is not as precise as with the DME. Also, the surfaces of fixed-surface electrodes become contaminated with adsorbed and electrodeposited materials. Thus, unlike the DME, they must be cleaned often. However, despite these limitations, fixed-surface electrodes have been successfully used in many applications, especially in the positive region, where mercury cannot be used. It is in this region where many organic oxidations take place.

CHRONOAMPEROMETRY

Definition

Chronoamperometry is a controlled potential technique in which the electrolysis of an analyte occurs at a stationary electrode in a quiescent solution. The electrode potential is suddenly stepped to some fixed value and the electrolysis current is displayed against time. Diffusion is the sole mode of mass transport.

Instrumentation

The instrument configuration for this technique is shown in Figure 23. The working electrode material may be any material which can be held stationary during the electrolysis. Since the solution must remain quiet, the cell should be mounted on a vibration-free support.
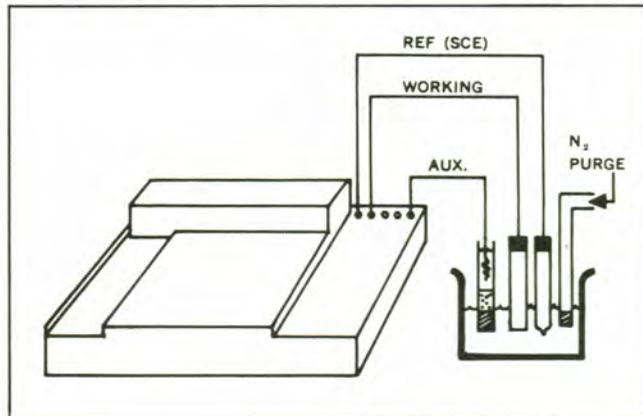
Figure 23. Instrumental Configuration for Chronoamperometry.

Principle

CURRENT TIME CURVE
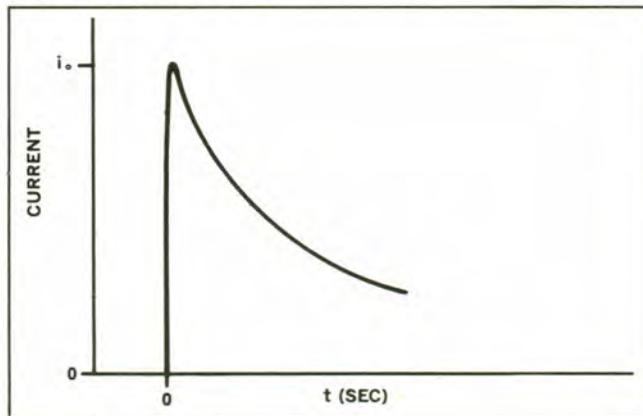
Figure 24. Typical Chronoamperogram.

A typical (i-t) curve is shown in Figure 24.

When time (t) equals zero, the potential of the working electrode in a quiet solution is suddenly stepped to some fixed value (E_{app}). If E is sufficient to cause electrolysis, the current suddenly increases from zero to some finite value (i_0). The current then decays as the electroactive species in the vicinity of the electrode is consumed.

INTERPRETATION OF CURRENT-TIME RELATIONSHIP

The electrolysis current is governed by the diffusion rate of the electrolyzed component and the electron transfer rate of the electrode reaction. If the applied potential is sufficiently large so that the rate constant k_c (or k_a) is

large (i.e., the electrolysis is diffusion controlled), then the resulting current is given by the Cottrell Equation:

$$i_d = \frac{nFAD^{1/2}}{\pi^{1/2}t^{1/2}} C_b \tag{49}$$

The only new term in this equation is t, which is the time (in seconds) after the controlled potential has been applied to the working electrode. In the case of a very reversible system, any applied potential greater than the decomposition potential of the system is sufficient to satisfy the above conditions. If the electrode potential is not sufficiently large to make the electrolysis current diffusion controlled, which is often the case with an irreversible system, the resulting current is given by:

$$i = i_d [\pi^{1/2}\lambda \exp (\lambda)^2 \operatorname{erfc} (\lambda)] \tag{50}$$

where

$$\lambda = k_c \frac{t^{1/2}}{D^{1/2}} \tag{51}$$

and

$$\operatorname{erfc}(\lambda) = 1 - \frac{2}{\pi^{1/2}} \int_0^\lambda e^{-z^2} dz \tag{52}$$

Applications

DIRECT QUANTITATIVE ANALYSIS

As can be seen from Equation 49, i_d is proportional to C_b. Accordingly, C_b can be calculated by selecting from the chronoamperogram a value $(i_d)_x$ corresponding to a value $(t)_x$ and substituting these in Equation 49.

KINETIC STUDIES

As can be seen from Equation 50, by selecting current-time values from the recorded trace and substituting them into this equation, k_c (or k_a) can be calculated for any applied potential.

Advantages and Limitations

For quantitative analysis as well as kinetic studies, chronoamperometry offers speed and simplicity. However, it does require a prior knowledge of the current-voltage characteristics of the electrochemical system. In the case of quantitative analysis, a potential must be chosen at which i will be diffusion controlled. On the other hand, when determining k_c (or k_a), potentials must be used near the foot of the i-E curve where i is not diffusion controlled.

POTENTIAL SWEEP CHRONOAMPEROMETRY AND CYCLIC VOLTAMMETRY

Definition

Potential sweep chronoamperometry is a controlled potential technique in which the electrolysis of an analyte occurs at a stationary electrode in a quiescent solution. In contrast to solid electrode voltammetry, diffu-

sion is the sole mode of mass transport and the working electrode potential is scanned linearly at a rapid rate (several mv/sec. to several hundred mv/sec.).

Cyclic voltammetry is an extension of the potential sweep technique in which the potential is swept back and forth over the same region several times.

Instrumentation

The instrumental configuration of this technique is shown in Figure 25. It is identical to that shown for chronoamperometry.
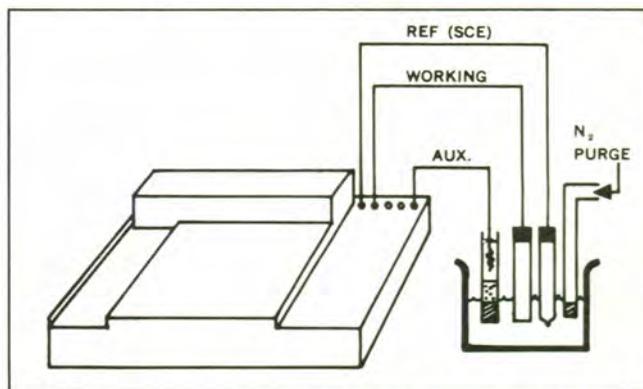
Figure 25. Instrumental Configuration for Potential Sweep Chronoamperometry and Cyclic Voltammetry.

Principle

TYPICAL CURRENT-POTENTIAL CURVE

A typical i-E curve is shown in Figure 26.
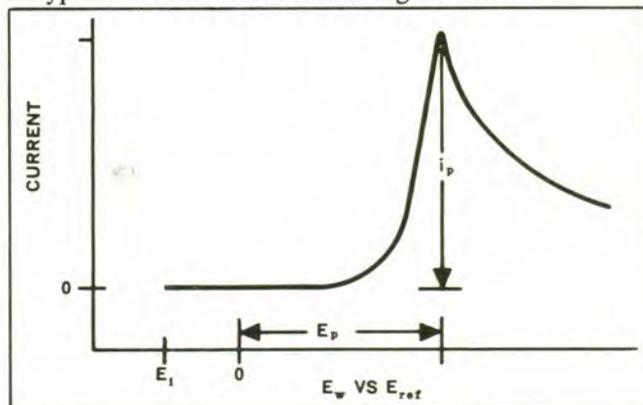
Figure 26. Typical i-E Curve.

If the working electrode potential is swept negatively, a current peak due to reduction results. Positive sweeps result in oxidation peaks. During the first part of the sweep, no current flows until the decomposition potential of the analyte is reached. Once this point is passed, the current rises rapidly as the analyte is consumed at the electrode surface. Since the solution is unstirred, the analyte concentration at the electrode surface is soon depleted, and the current begins to drop. This process is repeated when the potential is sufficient to electrolyze the next electroactive species.

CURRENT-POTENTIAL RELATIONSHIPS

If the electrode reaction is fast (reversible) and the reactants and products are soluble, then:

$$i_P = 2.72 \times 10^5 \, n^{3/2} \, AD^{1/2} \, C_b \, \nu^{1/2} \text{ at } 25°C \qquad (53)$$

where i_P is in amps and ν is the potential scan rate in volts/sec. If the electrolysis results in the deposition of an insoluble substance, the numerical constant in Equation 53 is 3.67×10^5. The relative position of the peak potential is:

$$E_P = E_{1/2} - 0.028/n \qquad (54)$$

where $E_{1/2}$ is the voltammetric half-wave potential. If the electrode reaction is slow (irreversible), then:

$$i_P = 3.01 \times 10^5 \, n(\alpha n_a)^{1/2} \, AD^{1/2} \, C_b \nu^{1/2} \text{ at } 25°C \qquad (55)$$

where n_a is the number of electrons in the rate-controlling step and α is the transfer coefficient. Consequently, the height of the current peak is affected by the electrode reaction rate.

During the initial current rise (up to 10% of i_P) the current is almost totally controlled by the kinetics of the electron transfer mechanism. In this region, the current is defined by:

$$i = nFAC_b k_s \exp\left[(\alpha n_a F/RT)(E_{app} - E_i)\right] \qquad (56)$$

where E_i equals the potential at the start of the sweep and E_{app} equals the potential of the working electrode at any given point in the potential sweep.

CYCLIC VOLTAMMETRY

If, at the end of one potential sweep, the sweep direction is reversed, electrolysis of the products of the forward sweep takes place. This technique is illustrated in Figure 27.
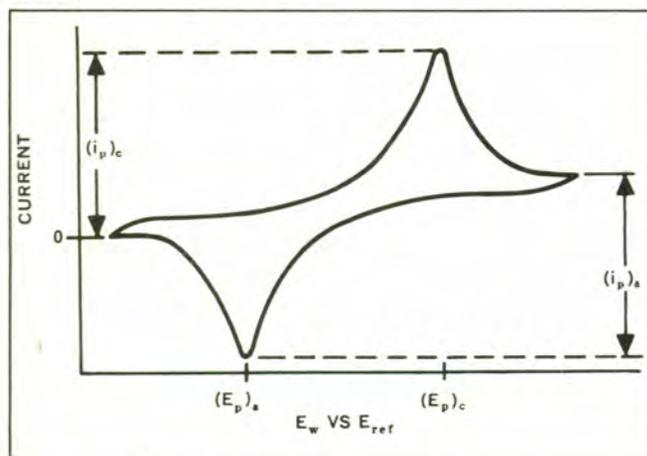
Figure 27. Cyclic Voltammogram.

For a reversible system:

$$(i_p)_c = (i_p)_a \qquad (57)$$

and the separation of these peaks are:

$$(E_p)_c - (E_p)_a = \Delta E_p = 60/n \text{ (mv)} \qquad (58)$$

For an irreversible system, the peak separation ΔE_p is related to ψ as shown in the following table where:

$$\Psi = k_s \left(\pi \frac{nF\nu D}{RT}\right)^{1/2} \qquad (59)$$

assuming $D_{Ox} \cong D_{Red} \qquad (60)$

Ψ	$n(\Delta E_p)$
20	61 mv
7	63
6	64
5	65
4	66
3	68
2	72
1	84
0.75	92

Figure 28. Variation of ΔE_p with ψ. (See BIBLIOGRAPHY FOR POTENTIAL SWEEP CHRONOAMPEROMETRY AND CYCLIC VOLTAMMETRY, page 34, reference 10.)

Applications

QUALITATIVE ANALYSIS

Since E_P is closely related to the $E_{1/2}$ of polarography, it has the same qualitative usefulness.

DIRECT QUANTITATIVE ANALYSIS

For a given electroactive species in a particular solvent, Equation 53 or 55 can be reduced to:

$$i_P = kC_b \qquad (61)$$

where k is the constant of proportionality which can be evaluated with standard solutions.

Sensitivity

For a reversible system, this technique is in the order of 10 times more sensitive than polarography. Often, distinct peaks can be detected at concentrations as low as 10^{-6} M. While the improvement for irreversible systems is less, there is a 5 to 10-fold improvement over polarography.

Selectivity

In general, the selectivity of this technique is the same as for polarography except for improved resolution. Species with $E_{1/2}$ values, differing by 100 mv, can usually be resolved.

Accuracy

The accuracy of this technique is approximately the same as for polarography. That is, about 5% if Equation 53 is used or 1-2% if careful standardization is used with Equation 61.

KINETIC STUDIES

It can be seen from Equation 56 that a plot of (ln i)

where i is less than 10% of i_p, versus $E_{app} - E_i$ will result in a line with a slope proportional to αn_a and an intercept proportional to k_s.

In the case of cyclic voltammetry, a scan rate (v) can be selected such that ΔE_p is measurably different from 60 mv. This ΔE_p can then be used to get ψ from the Table (Figure 28) and k_s can then be calculated from Equation 59.

Advantages and Limitations

Potential sweep chronoamperometry has a number of advantages over polarography. Resolution of substances with half-wave potentials lying close to each other can be more easily distinguished. Sensitivity is 5 to 10 times better. Speed is 10 to 20 seconds versus 10 to 15 minutes per scan. By using stationary electrodes rather than dropping electrodes, the technique is simpler than polarography. The advantages of potential range is the same as that cited for solid electrode voltammetry.

On the other hand, fixed-surface electrodes require careful maintenance in order to achieve repeatable results, and quantitative accuracies cited above are applicable to only the first species electrolyzed in a multicomponent system.

CONTROLLED POTENTIAL COULOMETRY

Definition

In coulometric analysis, a measurement is made of the quantity of electricity required to electrolyze a substance quantitatively and stoichiometrically at a working electrode in a well-stirred solution. In controlled potential coulometry, the potential of the working electrode is controlled at a constant value, and the electrolysis current is measured against time. Completion of the electrolysis is signaled by decay of the current to a negligibly small value.
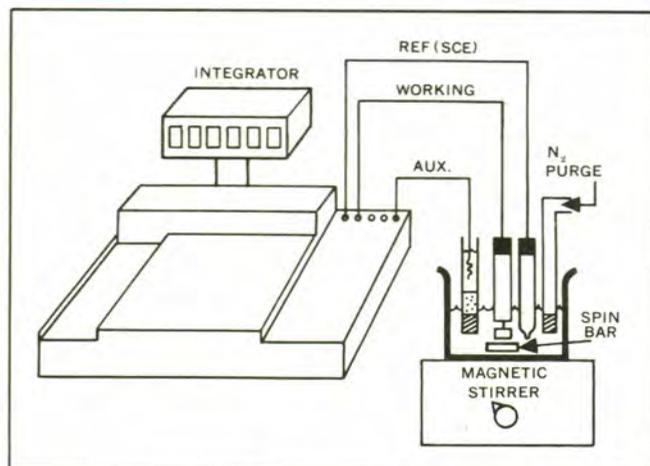
Figure 29. Instrumental Configuration for Controlled Potential Coulometry.

Instrumentation

The instrumental configuration for this technique is shown in Figure 29. Stirring is done either by rotating the electrode or by stirring the solution. Large-area working electrodes are usually used in order to speed up the electrolysis.

Principle

THE CURRENT-TIME CURVE

A typical current-time curve for controlled potential coulometry is shown in Figure 30.
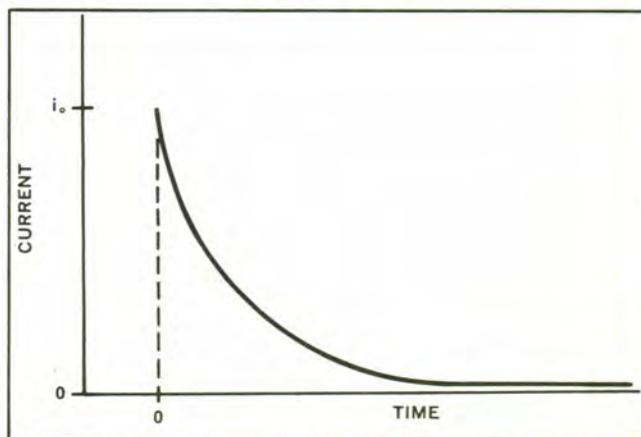
Figure 30. Typical i-t Curve for Controlled Potential Coulometry.

Before starting the electrolysis, the working electrode potential is chosen which will electrolyze the species of interest. If this potential is not known beforehand, it can be determined from a polarogram or voltammogram of a standard solution of the desired analyte.

When the electrolysis is begun, the current increases to an initial high level (i_o). It then decays exponentially as the analyte is consumed. The electrolysis is complete, for all practical purposes, when the current has decayed to less than 0.1% of the initial current.

INTERPRETATION OF THE CURRENT-TIME CURVE

The current decay in controlled potential coulometry is described by this equation:

$$i_t = i_o 10^{-Kt} \tag{62}$$

where i_o equals the initial current, i_t equals the current at time (t):

and $\quad K = 25.8 \, DA/Vol. \, \delta \tag{63}$

The constant K is inversely proportional to the time required for the electrolysis to reach any degree of completion. Thus, the electrolysis time can be made small by making the electrode area to solution volume ratio (A/Vol.) large and/or by making the diffusion layer δ small by rapid, efficient stirring.

The total amount of electricity (Q) which is required to

exhaustively electrolyze a certain species is the current-time integral:

$$Q = \int_0^t idt \qquad (64)$$

This integral is equal to the area under the i-t curve in Figure 30. The quantity (Q) is in turn related to the original concentration of the electrolyzed species according to Faraday's Law (see FARADAY'S LAW, page 8):

$$Q = nFVC_b \qquad (65)$$

where F equals 96,490 coulombs, V equals volume of solution (liters), and C_b equals bulk concentration of the electrolyzed analyte (moles/liter).

COULOMETERS

Integration of the i-t curve may be done by graphic, mechanical, electromechanical, or electronic means. A concise summary of these various methods of integration have been presented (see BIBLIOGRAPHY FOR CONTROLLED POTENTIAL COULOMETRY, page 34, reference 10).

One concise method of accomplishing integration is with a ball and disk integrator. This type of integration is described in detail (see BIBLIOGRAPHY FOR CONTROLLED POTENTIAL COULOMETRY, page 34, reference 2). Commercially-available units can be attached to the potentiometric recorder which draws the i-t curve. This type of integrator gives a continuous indication of the i-t integral.

Applications

DIRECT QUANTITATIVE ANALYSIS

The quantitative application of controlled potential coulometery depends upon Equation 65, which relates the current-time integral (Q) and the bulk concentration.

Sensitivity

Coulometry is particularly suited to the quantitative determination of small quantities of electrolyzable material. For example, a current of $1 \mu a$ flowing for 1 second is an amount of electricity equivalent to approximately 10^{-11} gram equivalents. Such an amount of electricity can be measured with reasonable accuracy.

Selectivity

The ability to electrolyze one species in the presence of another depends upon the relative position and separation of their half-wave potentials. In every case, it is the most oxidizable or the most reducible species which is electrolyzed selectively. If the most reactive species is followed by one whose half-wave potential is 0.4 volt more inert, a 99.99% separation can be accomplished. If $\Delta E_{1/2}$ is 0.2 volt, a separation of 99.5% is possible.

Accuracy

When the desired electrolysis proceeds with 100% cur-

rent efficiency (i.e., no side reactions), and adequate corrections are made for residual and non-Faradaic currents, the error of this technique approaches 0.1%.

When attempting to determine electro-kinetic constants, the value of n (the over-all number of electrons exchanged per molecule) must be known. This can be determined most reliably by measuring the coulombs necessary to electrolyze a known concentration of the system being studied and calculating n from Equation 65.

Advantages and Limitations

The combination of high accuracy and sensitivity makes controlled potential coulometry one of the most reliable and useful analytical techniques. Furthermore, no standard solutions are required, once a given procedure has been demonstrated to proceed with 100% current efficiency.

Two limitations of this technique are the need for an integrator and the lack of speed. Exhaustive electrolysis often requires several minutes.

CHRONOPOTENTIOMETRY

Definition

Chronopotentiometry is a controlled current technique in which the electrolysis of an analyte occurs at a stationary electrode in a quiescent solution. The cell current is suddenly stepped to some fixed value and the resulting working electrode potential displayed against time.

Reverse current chronopotentiometry is an extension of the basic technique. In reverse current chronopotentiometry, the polarity of the electrolysis current is reversed, resulting in electrolysis of the species previously produced at the electrode.

Instrumentation

The instrumental configuration is shown in Figure 31. The working electrode material may be any material which can be held stationary during the electrolysis. Since
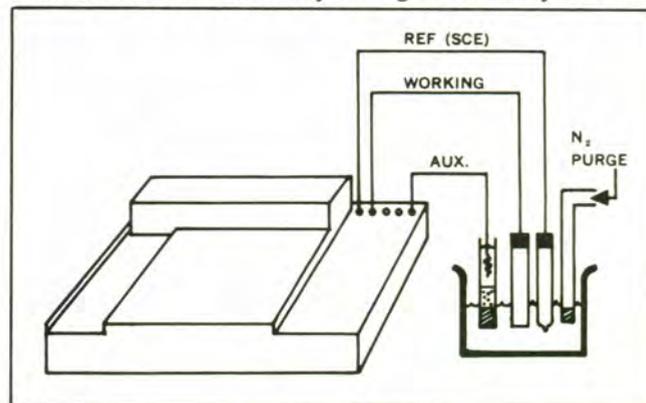
Figure 31. Instrumental Configuration for Chronopotentiometry.

the solution must remain quiet, the cell should be mounted on a vibration-free support.

Principle

POTENTIAL-TIME CURVES

A typical chronopotentiogram for a Fe^{+3} solution is shown in Figure 32.
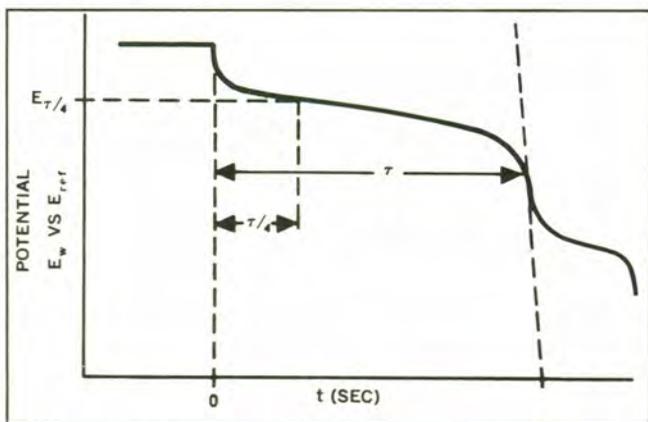
Figure 32. Typical Chronopotentiogram of the Reduction of Fe^{+3}.

At time (t) equals zero, the current through the electrolysis cell is suddenly stepped from zero to some fixed value i. Initially, the solution contains only Fe^{+3} ions. At the instant that a constant cathodic current is initiated, Fe^{+2} ions are produced at the electrode surface and the potential changes to a value in the vicinity of the standard potential for the Fe^{+3}/Fe^{+2} couple. As the current continues to flow, more and more Fe^{+2} ions are produced from the Fe^{+3} ions that diffuse to the electrode. Eventually, the rate of diffusion of Fe^{+3} to the electrode from the bulk of the solution becomes smaller than the rate of consumption of Fe^{+3} by the electrode reaction, so that the concentration of Fe^{+3} at the electrode surface becomes very small. At this point the electrode potential which depends on the ratio of the concentrations of Fe^{+3} and Fe^{+2} at the electrode surface, abruptly becomes much more negative. This rapid potential transition defines a time called the transition time. It is the time required for the electrode reaction to convert essentially all of the Fe^{+3} at the electrode surface to Fe^{+2}. This same process is repeated for the next electroactive species.

INTERPRETATION OF POTENTIAL TIME-CURVES

The fundamental equation for chronopotentiometry is the Sand Equation:

$$\tau^{1/2} = \left(\frac{\pi^{1/2}F}{2} \right) \left(\frac{A}{i} \right) \left(\frac{nD^{1/2}}{1} \right) C_b \qquad (66)$$

where τ, F, A, i, n, D, and C_b are the transition time (sec.), the Faraday (96,490), the area of the working electrode (cm^2), the constant current (μa), the number of electrons, the diffusion coefficient of the electroactive

species (cm^2/sec), and the bulk concentration of the latter (mF), respectively.

This equation, which is applicable to reversible and irreversible systems, is derived with the assumption that semi-infinite linear diffusion takes place.

A chronopotentiogram of a two-component system will have two potential transitions. The equation for the second transition is:

$$(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} = \left(\frac{\pi^{1/2}FA}{2} \right) \left(\frac{n_2 D_2^{1/2}}{1} \right) (C_b)_2 \qquad (67)$$

where the subscript (2) relates to the second component.

The working electrode potential (E_w) and the transition time (τ) for a reversible system are related as follows:

$$E_w = E_{\tau/4} + \frac{RT}{nF} \ln [(\tau/t)^{1/2} - 1] \qquad (68)$$

where E_w equals the potential at the working electrode, $E_{\tau/4}$ equals the potential at ¼ of the transition time and:

$$E_{\tau/4} = E^0 \qquad (69)$$

The potential-time equation for an irreversible system is:

$$E_w = \frac{RT}{\alpha n_a F} \ln \left(\frac{nFAC_b k_c}{1} \right) + \frac{RT}{\alpha n_a F} \ln [1 - (t/\tau)^{1/2}] \qquad (70)$$

REVERSE CURRENT CHRONOPOTENTIOMETRY

If the current polarity is reversed during the potential pause, a chronopotentiogram of the electrolysis products is obtained. The reverse current chronopotentiogram is pictured in Figure 33.
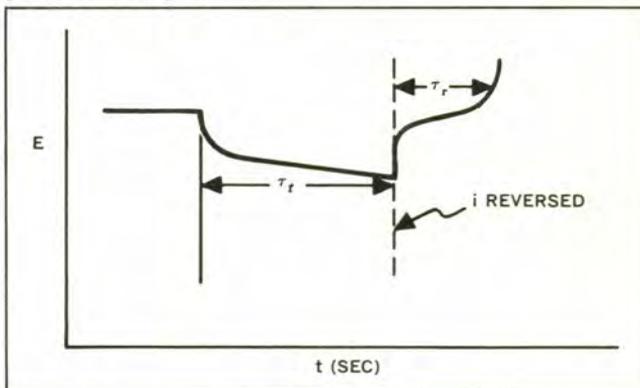
Figure 33. Current Reversal Chronopotentiometry.

If the electrolysis products are soluble:

$$\tau_t = \tfrac{1}{3}\tau_r \qquad (71)$$

If the products are insoluble:

$$\tau_t = \tau_r \qquad (72)$$

Applications

QUALITATIVE ANALYSIS

Since $E_{\tau/4}$ is related to the E^0 of potentiometry and the $E_{1/2}$ or polarography, it has the same qualitative usefulness.

DIRECT QUANTITATIVE ANALYSIS

When analyzing for a given electroactive species, with a fixed-area electrode, Equation 66 can be reduced to:

$$i\tau^{1/2} = kC_b \qquad (73)$$

where k is a proportionality constant which can be evaluated with standard solutions. The best results are usually obtained by changing i as C_b changes so as to keep τ in the 5 to 10 second range. Chronopotentiometry has been successfully applied to many organic and inorganic systems.

Sensitivity

Chronopotentiometry has about the same lower limit of sensitivity as polarography. This technique can often be used in solutions which are more concentrated than those suitable for polarography.

Selectivity

The comments concerning the selectivity of polarography apply here as well (see SELECTIVITY, page 16).

Accuracy

Numerous workers have demonstrated that this technique is more accurate than polarography. Many examples of accuracies of better than 1% have been reported.

KINETIC STUDIES

The kinetic factors k_c (or k_a) and αn_a can be derived from a chronopotentiogram using Equation 70. A plot of $\ln [1 - (t/\tau)^{1/2}]$ versus E_w yields a straight line whose slope is proportioned to αn_a, and whose E-intercept is proportional to k_c (or k_a).

ELECTROCHEMISTRY OF LABILE SUBSTANCES

Current reversal chronopotentiometry offers the chemist a unique tool for studying the electrochemical properties of labile substances. An otherwise unstable substance can be generated with a current of one polarity and then electrolyzed chronopotentiometrically before it decays by reversing the current polarity. This technique has also been useful in elucidating many reaction mechanisms.

Advantages and Limitations

The quantitative sensitivity and resolution of this technique is about the same as polarography. However, the advantages of speed, simplicity, and potential range cited for potential sweep chronoamperometry also apply here.

As in the case of cyclic voltammetry, current reversal chronopotentiometry is a very powerful and accurate tool for studying the electrochemical properties of labile substances.

The limitations of this technique are similar to those cited for potential sweep chronoamperometry. Fixed-surface electrodes require careful cleaning, and high quantitative accuracy is achieved only with the first species to be electrolyzed.

CONTROLLED CURRENT COULOMETRY (Coulometric Titrations)

Definition

Controlled current coulometry is a technique in which a constant cell current is used to generate a reagent in a well-stirred solution which will stoichiometrically titrate the substance to be determined. The potential of an indicator electrode is measured against time in order to locate the titration end point.

Instrumentation

The Electroscan 30 Electroanalytical System can be used for controlled current coulometric titrations utilizing the arrangement shown in Figure 34. The instrument controls the current through the cell to a constant, preset value and polarity. The potential of the indicating electrode is displayed against time on the recorder chart.
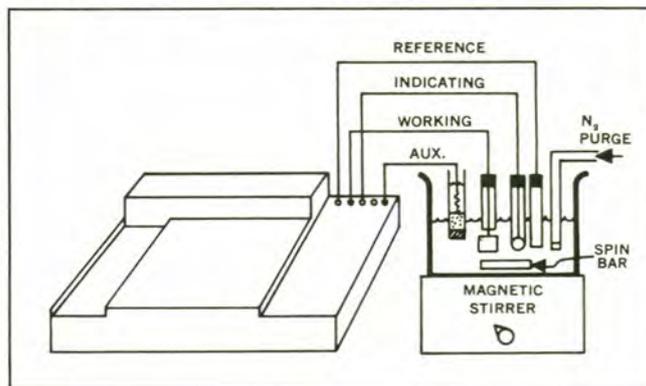
Figure 34. Instrumental Configuration for Controlled Current Coulometry.
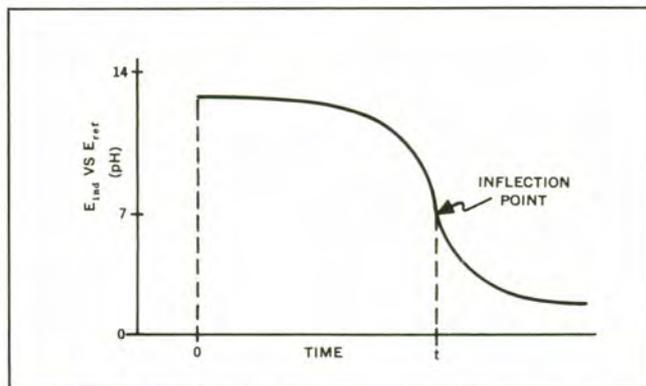
Figure 35. Coulometric Acid-Base Titration with Potentiometric Indication.

An example of a coulometric acid-base titration with a potentiometric indicating system is shown in Figure 35. The pH of the sample solution is initially high, because of an excess of OH^- ions. After the electrolysis (H^+ generation) begins, the pH drops, slowly at first, and then rapidly, as the titration is completed and an excess of H^+ ions is produced. The end point of the titration is located at the inflection point in the titration curve, which corresponds to time (t) in Figure 35.

Both the coulombs (Q) required to cause the titration of the sample and the concentration (C_b) of the sample may be calculated from the following equation:

$$Q = it = nFVC_b \qquad (74)$$

where i equals the constant generating current and t equals time (sec.) to reach the end point.

Titrant Generation

Before the titration is started, three things must be accomplished. First, an appropriate solvent must be found which will provide the components necessary to allow the electrochemical generation of the appropriate titrant. Second, the current level must be chosen so that the current density (i/A) at the working electrode surface will be sufficiently low to insure 100% current efficiency. Finally, the current polarity must also be chosen so that the appropriate titrant will be generated at the working electrode surface. For example, with platinum electrodes in an aqueous solution, a base may be generated by reduction of water at the cathode:

$$H_2O + e^- \rightarrow OH^- + \tfrac{1}{2} H_2 \qquad (75)$$
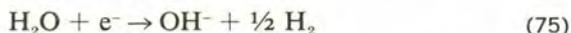
or an acid may be generated by oxidation of water at the anode:

$$\tfrac{1}{2} H_2O \rightarrow H^+ + \tfrac{1}{4} O_2 + e^- \qquad (76)$$

If the sample solution contains any substance which is more easily reduced (when a base is being generated) or oxidized (when an acid is being generated) than the solvent, water, then external generation must be employed (see BIBLIOGRAPHY FOR CONTROLLED CURRENT COULOMETRY, page 34, reference 10).

End Point Detection

Once the preliminary steps outlined above are taken, the coulometric titration is identical to a classic titration except the buret is replaced by the working electrode. The methods of end point detection are also identical to those used in ordinary titration procedures.

Applications
Quantitative Analysis by Titration

This technique has the same high accuracy and sensitivity as described for controlled potential coulometry. The selectivity of this technique is provided by the selectivity of the titrant generated.

Controlled current coulometry has been successfully employed in redox, acid-base, precipitation, and complexion titrations. It has also been successfully used to determine the thickness of metal and metal oxide surface films.

Advantages and Limitations

As in the case of controlled potential coulometry, accuracy and sensitivity are two of the outstanding features of this technique. Three additional advantages, which this technique shares with the controlled potential method, are no standard solutions are required; titrants too unstable to be stored, often may be coulometrically generated (e.g., Cl_2, Ag^{+2}, Cr^{+2}, etc.); and accurate standard solutions for other analytical techniques may be coulometrically generated.

The technique has two advantages over controlled potential coulometry. The 100% current efficiency is easier to achieve due to the selection of an appropriate solvent-electrolyte system, and determination of Q does not require an integrator.

The technique has two limitations. Not all titrants can be generated coulometrically, and an effective indicating system must be found in order to determine the titration end point.

ELECTRODEPOSITION AND SEPARATION

Definition

Electrodeposition and separation is a technique in which an insoluble deposit is formed electrochemically on a solid electrode or amalgamated with a mercury electrode. The complete electrolysis of a depositable species is usually carried out at a large surface area electrode in a well-stirred solution. The electrolysis may be carried out at either controlled potential or controlled current.
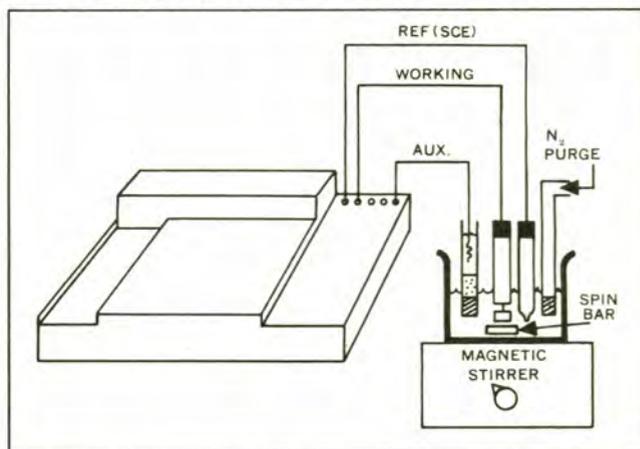
Figure 36. Instrumental Configuration for Electrodeposition and Separation.

Instrumentation

The instrumental configuration for this technique is shown in Figure 36. Stirring is done either by rotating the electrode or by stirring the solution. Large area working electrodes are usually used in order to speed up the electrolysis.

Principle

Several cations (e.g., Fe^{+3}, Co^{+2}, Ni^{+2}, etc.) can be electrolytically reduced to their metallic state and deposited onto or into an electrode. The usual objectives of this technique are quantitative determination of a depositable species by weighing the resulting deposit (electrogravimetry); deposition to secure a separation of the deposited species from the rest of the solution (electroseparation); and electrolytic deposition for preparative purposes (electroplating).

CONTROLLED POTENTIAL ELECTRODEPOSITION

Before starting the electrolysis, the working electrode potential is set large enough to electrolytically deposit the species of interest but not so large as to deposit the next most electroactive species. If this potential is not known beforehand, it can be determined from a polarogram or voltammogram of a standard solution of the desired species. The potential is usually set 0.1 to 0.2 volt more negative than the half-wave potential of the species.

This form of electrodeposition is the same as controlled potential coulometry (CPC) except that the objective is securing a deposit rather than measuring coulombs. As in CPC, the initial current is high as electrolysis is begun, but decays to zero as the deposition goes to completion. Several species can be deposited sequentially by advancing the working electrode potential as each deposition is completed.

CONTROLLED CURRENT ELECTRODEPOSITION

In this technique a fixed cathodic current is applied to the electrolysis cell and the plating-out of the most easily deposited species takes place. When only one depositable species is present, this method is faster than the controlled potential method. However, when there are several depositable materials present, special techniques must be used in order to insure selective deposition. In such cases, controlled potential deposition often offers the best compromise between speed and selectivity.

Applications

DIRECT QUANTITATIVE ANALYSIS

The amount of a substance in solution may be determined by weighing the working electrode before and after exhaustively depositing it from solution.

SEPARATION

Electrodeposition has been used to remove unwanted materials from solution prior to electrochemical, spectrographic, and spectrophotometric analysis. It has also been used for separating radioactive isotopes from other elements and as an aid in analyzing exchange rates of radioactive elements.

Advantages and Limitations

A high degree of selectivity and accuracy can be achieved by electrogravimetric analysis if the amount of analyte deposited is sufficient to be weighed accurately. Electrodeposition often results in a 99.9% separation of the desired species from solution. This degree of separation is hard to achieve by other separation techniques.

The major limitation of this technique is that it is only applicable to elements which form stable deposits on or in an electrode.

SECTION 4...SUMMARY

ELECTROANALYTICAL TECHNIQUES

When using electrochemical techniques for chemical analysis, the potential at an electrode surface (E_a) is a function of the concentration of some analyte (C), the current that may flow during the measurement (i), a time function (t), and any mass transport rate (MTR) that might exist at the electrode and the area (A) of the electrode.

As illustrated in the following table, electroanalytical techniques can be classified according to which terms are controlled and which are measured.

SUMMARY OF ELECTROANALYTICAL METHODS

	PARAMETER CONTROLLED	VARIABLE MEASURED
CONTROLLED CURRENT METHODS		
Potentiometry	Zero i	E
Potentiometric Titration	Zero i and titrant addition	E vs Vol.
Potentiometric Titration (one or two polarized electrodes)	Constant i and titrant addition	E vs Vol.
Controlled Current Coulometric Titration, with Potentiometric Indication	Constant i to produce titrant from appropriate solvent	E vs t, where t equiv. to titrant
Chronopotentiometry	Constant i	E vs t
Constant-Current Electrogravimetry	Constant i	Weight of Deposit
CONTROLLED POTENTIAL METHODS		
Polarography	Constant E or Linear Sweep E	i vs E
Voltammetry	Constant E or Linear Sweep E	i vs E
Amperometric Titration (one or two polarized electrodes)	Constant E and titrant addition	i vs Vol.
A.C. Polarography	Linear Sweep E + Sinusoidal E (small amplitude)	i_{AC} vs E_{sweep}
Chronoamperometry	Constant E	i vs t
Potential Sweep Chronoamperometry	Linear Sweep E	i vs E
Cyclic Voltammetry	Triangular Sweep E	i vs E
Controlled E Electrogravimetry	Constant E	Weight of Deposit
Controlled E Coulometry	Constant E	i vs t

MASS TRANSPORT RATE	ANALYTICAL SIGNIFICANCE	TYPICAL TRACE
Incidental	$E = E^0 + \dfrac{RT}{nF} \ln \dfrac{a_{Ox}}{a_{Red}}$	Meter or recorder deflection
Fast (stirred solution)	Vol. $\alpha\, C_b$	
Fast (stirred solution)	Vol. $\alpha\, C_b$	
Fast (stirred solution)	$Q = i \triangle t \, \alpha\, C_b$	
Slow (diffusion controlled)	$\tau^{1/2} \, \alpha\, C_b$	
Fast (stirred solution)	Wt $\alpha\, C_b$ (Vol.)	None
Controlled by diffusion and DME	$i_d \, \alpha\, C_b$	
Fast (rotating electrode)	$i_{lim} \, \alpha\, C_b$	
Fast (stirred solution)	Vol. $\alpha\, C_b$	
Controlled by diffusion and DME	$i_D \, \alpha\, C_b$	
Slow (diffusion controlled)	$i_t \, \alpha\, C_b$	
Slow (diffusion controlled)	$i_p \, \alpha\, C_b$	
Slow (diffusion controlled)		
Fast (stirred solution)	Wt $\alpha\, C_b$ (Vol.)	None
Fast (stirred solution)	$Q = \displaystyle\int_o^t i \, dt \, \alpha\, C_b$ (Vol.)	
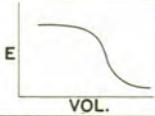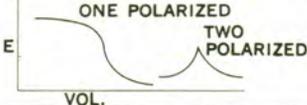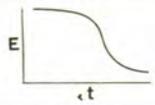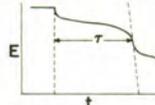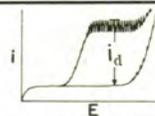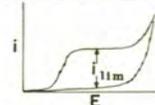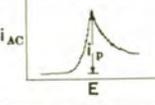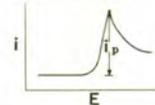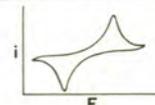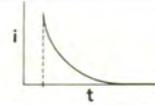
SECTION 5...INDEX OF SYMBOLS

A	Area (cm^2)
a	Activity
Ag, AgCl	Silver, Silver chloride electrode
AMP	Amplifier
α	Transfer coefficient
C	Concentration
C_b	Bulk concentration
$C°_{Ox}$, $C°_{Red}$	Concentration of oxidized and reduced species at the electrode surface
D	Diffusion coefficient (cm^2/sec)
D_{Ox}, D_{Red}	Diffusion coefficient of oxidized and reduced species
DME	Dropping mercury electrode
δ	Thickness of diffusion layer (cm)
E	Electrical potential
E°	Electrical potential under standard conditions
$E°_e$	Standard equilibrium potential
$E°'$	Formal standard potential
ε	A constant similar to E°
e^-	Electron
E_{app}	Applied voltage
$E_{1/2}$	Half-wave potential
E_{dme}	Dropping mercury electrode potential
E_{eq}	Equilibrium potential
E_{Ex}	External voltage
E_i	Potential at the start of a potential scan
E_{in}	Input voltage
erfc(x)	Error function compliment of x
E_p	Peak potential (volts)
$(E_p)_a$, $(E_p)_c$	Anodic and cathodic peak potential
E_q	Number of chemical equivalents
E_r	Reference voltage
E_s	Scan voltage
$E_{\tau/4}$	Chronopotentiometric quarter-wave potential
ETR	Electron transfer rate
E_w	Working electrode potential
exp(x)	e^x
$\triangle E_p$	Peak potential separation
f	Activity coefficient
F	Faraday's Constant (96,490 coulombs/equivalent)
i	Current (amp or μamp)
i_a	Current due to anodic (oxidation) reaction
i_c	Current due to cathodic (reduction) reaction
i_d	Diffusion current
I	Diffusion current constant

$(i_d)_a$, $(i_d)_c$	Anodic and cathodic diffusion current
$(i_d)_{ave}$	Average diffusion current at DME
$(i_d)_{max}$	Diffusion current at maximum drop life
i_f	Feedback current
i_{lim}	Limiting current
i_n	Net current at an electrode
i_o	Initial current
$(i_p)_a$, $(i_p)_c$	Anodic and cathodic peak current
i_r	Residual current
i_t	Current at time (t)
k	Proportionality constant
k_a, k_c	Rate constant for anodic and cathodic reaction
$k°_a$, $k°_c$	Formal anodic and cathodic rate constants
k_s	Standard rate constant
K	Mass transport constant
K_{sp}	Solubility product constant
ln x	Logarithm of x to the base e
log x	Logarithm of x to the base 10
M	Average mercury flow rate (mg/sec)
M_{rot}	Mass transport coefficient for a rotating electrode
MTR	Mass transport rate
n	Number of electrons exchanged per molecule of the electroactive species
n_a	Number of electrons exchanged in the rate-controlling step
η	Overvoltage
Ox	Oxidized form
pCl	Inverse logarithm of the chloride ion activity
pH	Inverse logarithm of the hydrogen ion activity
pNa	Inverse logarithm of the sodium ion activity
π	3.1416
R	Gas constant
R_c	Cell resistance
Red	Reduced form
R_f	Feedback resistor
R_r	Recorder resistor
SCE	Saturated calomel electrode
Q	Coulombs (amp-sec)
T	Temperature in °A
t	Time (sec)
t	Drop time (sec)
τ	Chronopotentiometric transition time (sec)
τ_f, τ_r	Forward and reverse transition times
v	Potential scan rate (volts/sec)
Vol, V	Volume of solution being electrolyzed

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SECTION 6...BIBLIOGRAPHY

The following bibliography provides specific and detailed information for more intensive study within each of the electroanalytical techniques discussed. For your convenience, they have been grouped according to technique.

POTENTIOMETRY

1. Bates, R. G., *Determination of pH, Theory and Practice*. New York: Wiley, 1964.
2. Delahay, P., *Instrumental Analysis*. New York: MacMillan Co., 1957, pp. 9-63.
3. Dole, M., *The Glass Electrode*. New York: Wiley, 1941.
4. Furman, N. H., *Anal. Chem.* (Review), 1950, Vol. 22, p. 33; 1951, Vol. 23, p. 21; 1954, Vol. 26, p. 84.
5. Kolthoff. I. M. and P. J. Elving, *Treatise on Analytical Chemistry*. New York: Interscience, 1963, Part 1, Vol. 4, Sec. D-2, pp. 2166-2170, 2181-2187, and 2270-2300.
6. Kolthoff, I. M. and N. H. Furman, *Potentiometric Titrations* (2nd Edition). New York: Wiley, 1932.
7. Lingane, J. J., *Electroanalytical Chemistry* (2nd Edition). New York: Interscience, 1958, pp. 36-168.
8. Reilley, C. N., *Anal. Chem.* (Review), 1956, Vol. 28, p. 671; 1958, Vol. 30, p. 765; 1960, Vol. 32, p. 185R.
9. Reilley, C. N. and R. W. Murray, *Anal. Chem.* (Review), 1962, Vol. 34, p. 313R; 1964, Vol. 36, p. 370R.

POLAROGRAPHY

1. Delahay, P., *New Instrumental Methods in Electrochemistry*. New York: Interscience, 1954.
2. Kolthoff, I. M. and J. J. Lingane, *Polarography* (2nd Edition). New York: Interscience, 1952.
3. Kolthoff, I. M. and P. J. Elving, *Treatise on Analytical Chemistry*. New York: Interscience, 1963, Part 1, Vol. 4, Sec. D-2, Ch. 46.
4. Lingane, J. J., *Electroanalytical Chemistry* (2nd Edition). New York: Interscience, 1958, p. 234.

5. Meites, L., *Polarographic Techniques* (2nd edition). New York: Wiley, 1965.
6. Milner, G. W. C., *The Principles and Applications of Polarography and Other Electroanalytical Processes*. Longmans, Green, New York, 1957.
7. Milner, G. W. C. and L. J. Slee, *Ind. Chemist.*, 1957, Vol. 33, p. 494.
8. Nurnberg, H. W. and M. J. von Stackelberg, *J. Electroanal. Chem.*, 1961, Vol. 2, pp. 181-350; 1962, Vol. 4, p. 1.
9. Schmidt, H. and M. J. von Stackelberg, *Modern Polarographic Methods*. New York: Academic Press, 1963.
10. Weissberger, A., *Techniques of Organic Chemistry: Physical Methods* (3rd Edition). New York: Interscience, 1960, Vol. 1, p. 3155.
11. Zuman, P. and I. M. Kolthoff, *Progress in Polarography*. New York: Interscience, 1962, Vols. 1 and 2.

SOLID ELECTRODE VOLTAMMETRY

1. Kolthoff, I. M. and P. J. Elving, *Treatise on Analytical Chemistry*. New York: Interscience, 1963, Part 1, Vol. 4, Sec. D-2, Ch. 47.
2. Kolthoff, I. M. and J. Jordan, *J. Am. Chem. Soc.*, 1954, Vol. 76, p. 3843.
3. Laitinen, H. A. and I. M. Kolthoff, *J. Phys. Chem.*, 1941, Vol. 45, pp. 1061-1079.
4. Zuman, P. and I. M. Kolthoff, *Progress in Polarography*. New York: Interscience, 1962, Vol. 2, p. 503.

CHRONOAMPEROMETRY

1. Delahay, P., *New Instrumental Methods in Electrochemistry*. New York: Interscience, 1954, Ch. 8.
2. Kolthoff, I. M. and P. J. Elving, *Treatise on Analytical Chemistry*. New York: Interscience, Part 1, Vol. 4, Sec. D-2, Ch. 44.
3. Lingane, J. J., *Anal. Chem.*, 1964, Vol. 36, p. 1723.
4. Murray, R. W. and C. N. Reilley, *J. Electroanal. Chem.*, 1962, Vol. 3, pp. 64 and 182.

POTENTIAL SWEEP CHRONOAMPEROMETRY AND CYCLIC VOLTAMMETRY

1. Kolthoff, I. M. and P. J. Elving, *Treatise on Analytical Chemistry*. New York: Interscience, 1963, Part 1, Vol. 4, Sec. D-2, Ch. 47.
2. Manning, D. L., *J. Electroanal. Chem.*, 1964, Vol. 7, pp. 302-306.
3. Miller, F. J. and H. E. Zittel, *J. Electroanal. Chem.*, 1964, Vol. 7, pp. 116-122.
4. Nicholson, R. S. and I. Shain, *Anal. Chem.*, 1964, Vol. 36.
5. Nicholson, R. S., *Anal. Chem.*, 1965, Vol. 37, p. 1353.
6. Ross, J. W., R. D. DeMars, and I. Shain, *Anal. Chem.*, 1956, Vol. 28, p. 1768.
7. Saveant, J. M. and E. Vianello, *Electrochemica Acta.*, 1965, Vol. 10, p. 905.
8. Streuli, C. A. and W. D. Cooke, *Anal. Chem.*, 1953, Vol. 25, p. 1691; 1954, Vol. 26, p. 963.
9. Zuman, P. and I. M. Kolthoff, *Progress in Polarography*. New York: Interscience, 1962, Vol. 2, p. 429.
10. Nicholson, R. S., *Anal. Chem.*, 1965, Vol. 37, p. 1353.

CONTROLLED POTENTIAL COULOMETRY

1. Jones, A. G., *Analytical Chemistry: Some New Techniques*. New York: Academic Press, 1959.
2. Kies, H. L., *J. Electroanal. Chem.*, 1962, Vol. 4, p. 257.
3. Kolthoff, I. M. and P. J. Elving, *Treatise on Analytical Chemistry*, New York: Interscience, 1963, Part 1, Vol. 4, Sec. D-2, Ch. 49.
4. Lewis, D. T., *Analyst*, 1961, Vol. 86, p. 494.
5. Lingane, J. J., *Electroanalytical Chemistry* (2nd Edition). New York: Interscience, 1958, Ch. 19-21.
6. Page, J. A., J. A. Maxwell, and R. P. Graham, *Analyst*, 1962, Vol. 87, p. 245.

7. Rechnitz, G. A., *Controlled Potential Analysis*. London: Pergamon, 1963.
8. Reilley, C. N., *Proc. Intern. Symposium Microchem.*, Birmingham University, Birmingham, Alabama, 1958.
9. Weissberger, A., *Technique of Organic Chemistry: Physical Methods*. New York: Interscience, 1960, Vol. 1, Part 4, Ch. 49.
10. Yoe, J. H. and H. J. Koch, *Trace Analysis*. New York: Wiley, 1957.

CHRONOPOTENTIOMETRY

1. Kolthoff, I. M. and P. J. Elving, *Treatise on Analytical Chemistry*, New York: Interscience, 1963, Part 1, Vol. 4, Sec. D-2, Ch. 44.
2. Lingane, J. J., "Analytical Aspects of Chronopotentiometry," *Analyst*, 1966, Vol. 91, pp. 1-9.
3. Lingane, J. J., *Electroanalytical Chemistry* (2nd Edition), New York: Interscience, 1958, Ch. 22.

CONTROLLED CURRENT COULOMETRY

See bibliography for Controlled Potential Coulometry, above.

ELECTRODEPOSITION AND SEPARATION

1. Alfonsi, B., *Anal. Chim. Acta.*, 1958, Vol. 19, pp. 276-283, 389-394, 569-575; 1959, Vol. 20, pp. 277-282.
2. Herringshaw, J. E. and Z. M. Kassir, *Analyst*, 1962, Vol. 87, p. 923.
3. Kolthoff, I. M. and P. J. Elving, *Treatise on Analytical Chemistry*. New York: Interscience, 1963, Part 1, Vol. 4, Sec. D-2, Ch. 48.
4. Lingane, J. J., *J. Electroanal. Chem.* (2nd Edition). New York: Interscience, 1958, Ch. 14-16.
5. Meites, L., *Handbook of Analytical Chemistry*. New York: McGraw-Hill, 1963, Sec. 5, p. 170.