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ELECTRODE KINETICS

by

John P. Elder

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John P. Elder

Chemical Engineering Division

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NOMENCLATURE

A	Electrode area	R_t	Total cell and circuit resistance
C	Capacitance	s	Laplace transform parameter, Eq. (47)
c	Concentration, capacity per unit electrode surface area	Sc	Schmidt number, Eq. (6)
c_b	Concentration in bulk solution, c_{O_b} and c_{R_b} , that of oxidized and reduced species, respectively	T	Absolute temperature
c_{dl}	Differential double-layer capacity per unit electrode surface area	t	Time, transport number, Eqs. (3-5), (8)
c_e	Concentration at electrode surface	V	Voltage
D	Diffusion coefficient, diameter	V_0	Sinusoidal voltage amplitude
$\vec{D}, \hat{D}$	Displacement and complex displacement vectors, Eqs. (114) and (117a), respectively	V_{ofd}	Faradaic-distortion voltage amplitude, Eq. (149)
E	Working potential	V_{fd}	Faradaic-distortion voltage, Eq. (154)
E_e	Equilibrium potential	v_c	Voltage output of power supply, Eq. (38)
E_e^0	Standard equilibrium potential	W	Warburg impedance, Eq. (107)
E_i	Electrode potential at current density, i	X, X_c	Capacitive reactance
$\vec{E}, \hat{E}$	Field-strength and complex-field-strength vectors, Eqs. (113) and (117a), respectively	x	Distance from electrode surface
F	Faraday	y	Local electrode height, Eqs. (5), (7a), and (8)
g	Acceleration due to gravity	Z	Impedance
Gr_h	Maximum Grashof number, Eq. (7b)	Z_f	Faradaic impedance
Gr_y	Local Grashof number, Eq. (7a)	z	Valence
Gr_z^0	Modified local Grashof number, Eq. (8)	α	Transfer coefficient, specific densification coefficient, $d(\ln \rho)/dc$
h	Electrode height, Eq. (7b); Planck's constant	β	Symmetry factor
I	Current	ΔE_{dl}	Nonfaradaic rectification voltage
I_{dl}	Double-layer charging current	ΔE_t	Faradaic rectification voltage at time t
I_f	Faradaic current	ΔE_∞	Faradaic rectification voltage at $t \rightarrow \infty$
i	Current density	$\Delta G_e^\#$	Free energy change at equilibrium potential
i_{dl}	Double-layer charging current density	Δq	Charge step
i_f	Faradaic current density	ΔV	Voltage step
i^0	Exchange current density	ϵ	Permittivity
i_A^0	Apparent exchange current density	η	Overpotential
i_m^0	Measured exchange current density	η_{act}	Activation overpotential
i_{lim}	Limiting current density	η_{conc}	Concentration overpotential
i_R	Faradaic rectification current density	η_{ct}	Charge-transfer overpotential
K	Equilibrium constant	η_{mt}	Mass-transfer overpotential
k	Boltzman constant, rate constant	η_Ω	Ohmic overpotential
k_e	Specific rate constant at equilibrium potential	θ	Phase angle
k^0	Standard rate constant	κ	Specific conductivity
k_A^0	Apparent standard rate constant	Δ	Equivalent conductivity
n	Number of electrons involved in overall electrode reaction	λ	Electron number
O	Oxidized species	μ	Chemical potential
$\vec{P}$	Polarization vector, Eq. (112)	$\bar{\mu}$	Electrochemical potential
p^1, p^0	Forward and backward reaction rate orders for oxidized species, Eq. (14)	ν	Stoichiometric number, kinematic viscosity (dynamic viscosity/density), Eqs. (6-8)
q^1, q^0	Forward and backward reaction rate orders for reduced species, Eq. (14)	ρ	Volume-charge density, density
R	Gas constant, reduced species, resistance	σ	Surface-charge density
R_c	Cell resistance	τ	Transition time, relaxation time
R_{ct}	Charge-transfer resistance, Eq. (34)	τ_{ct}	Charge-transfer relaxation, Eq. (90)
R_{mt}	Mass-transfer resistance, Eq. (105)	τ_D	Diffusional relaxation time, Eq. (92)
R_0, R_∞	Resistance parameters, Eqs. (129-131)	ϕ	Inner potential
		ω	Angular frequency

ELECTRODE KINETICS

by

John P. Elder*

I. INTRODUCTION

A complete understanding of the mechanism of any electrode reaction requires:

- a. A knowledge of the state of solvation of the electroactive species, and the environmental effect of all other species on the transport properties of the electroactive species.
- b. A precise description of the structure and properties of the electrochemical double layer, contiguous with the electrode surface.
- c. A thorough knowledge of the lattice structure of the electrode material.
- d. A knowledge of the causes and effects of any kinetic slow stage in the overall electrode process, before, during, or after the charge-transfer process.

This report deals exclusively with the last-mentioned topic. The modern concept of electrode kinetics will be outlined, followed by a consideration of the theoretical principles underlying the experimental techniques involved in the various sophisticated methods of investigating electrode kinetics at present.

II. ELECTRODE POLARIZATION AND OVERPOTENTIAL

If, when an electrode process occurs at a finite rate, there is a departure from the thermodynamic equilibrium potential, the electrode is said to be polarized. The measure of this polarization at any particular rate (current density) is referred to as the overpotential, defined as

$$\eta = |E_i - E_e|, \quad (1)$$

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where E_i is the observed electrode potential at a current density, i , and E_e is the formal equilibrium potential, both measured with respect to some arbitrary reference electrode system.

III. REFERENCE-ELECTRODE SYSTEMS

In all aqueous systems, the fundamental reference is the reversible hydrogen electrode. The reaction potential, corresponding to the equilibrium

with the pressure of hydrogen and hydrogen ion activity both equal to unity, is taken to be zero. In practice, various secondary electrode systems are employed. The saturated calomel, the glass, and the quinhydrone electrodes are three well-known examples. The theory and practice of such reference systems in both aqueous and nonaqueous solvents has been discussed in detail by Ives and Janz.¹ The requirements for a reliable reference-electrode system are reversibility and adequate reproducibility. In molten metal-molten salt systems, high temperature, mutual solubility of electrode and electrolyte, and the attendant corrosion problems make these requirements impracticable. Attempts have been made to produce a universal reference-electrode system for use with fused salts, without any great success. In most cases, when highly reactive molten metals and salts are to be used, the reference electrode has to be chosen on a basis of compatibility with the system. The one chosen is often a counterpart of one of the working electrodes, usually the most reactive. This field has been surveyed by both Laity (Chap. 12 of Ref. 1) and Delimarskii and Markov.²

IV. POLARIZATION PHENOMENA

Up to about 1950, an electrode process was said to be under activation control, if the slow stage was concerned with the charge transfer, because of the association of the slow reaction rate with the surmounting of a potential energy barrier involving a transient activated state. It has since been realized that certain homogeneous or heterogeneous chemical reactions may couple with the charge-transfer process to produce a polarizing effect. This has been termed reaction polarization, which, together with charge-transfer polarization, contributes to activation polarization.

Similarly, if the rate-determining step is associated with the transport of species between the electrode-electrolyte interface and the bulk solution, the process was said to be diffusion-controlled, the overall rate being dependent upon the magnitude of the concentration gradient across the so-called diffusion layer. Only when transient electrolyses are performed,

can one assume that diffusion is the sole mass-transfer phenomenon. Under all other conditions, natural convection and, under certain conditions, migration also make a significant contribution to mass transport. As a result of reaction polarization, there may be a slow supply of reactants or a slow removal of products from the reaction zone. This, together with mass-transfer polarization, constitutes concentration polarization.

There exists a spurious polarization effect, which results if an ohmic potential difference is included in the measured electrode potential. This occurs when anode-cathode current lines pass through the region in which the potential of the working electrode is measured with respect to the chosen reference electrode, or if a resistive film covers the working electrode surface. The ohmic overpotential is then given by the IR_c drop between the working and reference electrodes.

The three polarization effects (activation, concentration, and ohmic) may be distinguished by the manner in which they decay after the polarizing current closes: η_Ω decays instantaneously, η_{act} decays exponentially, and η_{conc} decays slowly and in a complex manner.

V. OHMIC OVERPOTENTIAL

In an experimental investigation, one should always attempt to obviate the spurious polarization effect mentioned above. The methods utilized for obviating this spurious effect are the direct and indirect (or interrupter) methods.

A. The Direct Method

The reference may be located external to, or it may be immersed in the bulk solution of, the working cell. In either case, it must be connected electrolytically with the solution at the working electrode-electrolyte interface. The capillary probe leading from a salt-bridge, joining the externally-located reference system, or directly from the reference-electrode compartment in the bulk solution of the working cell, to the electrode interface, is referred to as the Luggin-Haber capillary. If the probe is cylindrical in shape with diameter, D cm, located a distance, L cm, from the electrode surface, and if the bulk-solution specific and equivalent conductivities are κ and Λ , respectively, then the ohmic overpotential is given by³

$$\eta_\Omega = \frac{iD}{2\kappa} \ln \left[\frac{2L}{D} + 1 \right] + \frac{DF}{\Lambda(1-t)} \ln \left[1 - \frac{i}{i_{lim}} \right], \quad (3)$$

where i_{lim} is the limiting current density for the particular process, and t is the transport number of the appropriate electroactive species.

A study of the kinetics of metal deposition contained claims that the position of such a probe has importance with regard to current screening, and capillaries with lateral holes have been used.⁴ If a backside capillary⁵ is used, η_{Ω} may be reduced to a minimum. A narrow hole is drilled through the electrode, and the probe is inserted from the rear, the capillary orifice lying flush with the electrode surface. With this arrangement, there is no current screening and there is negligible disturbance of natural convective flow, which determines the concentration profile at the electrode-electrolyte interface.

B. The Indirect Method

The theory of the interrupter method, which was first championed by Newbery^{6,7} (see also Knobel, Caplan, and Eiseman⁸), is as follows: The working electrode is polarized by passing through the cell a constant current, which is interrupted for short periods of time at specified intervals. During the interruption period, there is no IR_C contribution to the potential difference between working and reference electrodes. The minimum potential attained during the interruption is measured for varying interruption times. The correct working electrode potential is evaluated by extrapolating to zero time interval. Hickling^{9,10} designed the first electronic commutator involving thyatron circuitry. He was able to measure potentials with an accuracy of ± 0.01 V in intervals of $5 \cdot 10^{-5}$ sec. Yeager, Hovorka, and their co-workers¹¹⁻¹³ have improved the design of the commutator circuit, increasing the accuracy to ± 0.005 V with interruption periods of $5 \cdot 10^{-6}$ sec. Cairns and Tevebaugh¹⁴ recently designed a simple interrupter unit, which behaves admirably. At this time, however, no details are available.

Regarding electrode kinetic studies in aqueous media, relatively few investigators have employed the indirect method because of the relative simplicity of the direct method. Luggin-Haber capillaries have been employed in electrode kinetic investigations in fused-salt media. However, many investigators assume that, because of the relatively low electrolyte resistance, one can neglect the IR_C drop, except at high current densities.

VI. MASS-TRANSFER OVERPOTENTIAL AND THE LIMITING CURRENT DENSITY

During any electrolysis, the concentrations of all species present in solution, in a region contiguous with the electrode-electrolyte interface, differ from those in the bulk solution. A natural consequence is that the resulting density changes effect a macroscopic convective fluid flow in this region. A balance is quickly set up between the various forces at play, and a steady-state concentration gradient is built up across this region, which is referred to as the "diffusion boundary layer." The thickness of this layer depends

upon certain flow parameters and property values (diffusion coefficient, dynamic viscosity, density, and ionic transport number) of the electrolyte system. It is usually of the order of magnitude 10^{-4} - 10^{-1} cm and, hence, need not be confused with the electrochemical double layer. The rate of mass transfer, which governs the mass transfer overpotential and the limiting current density, is dependent upon the thickness of the diffusion boundary layer. To evaluate η_{mt} at any particular current density i , and the average i_{lim} in terms of hydrodynamic factors, one must solve the complete equations of change for the system. This can only be carried out for relatively simple electrode geometries, as it involves solving coupled nonlinear differential equations. Various analyses have been given for plane-plate electrodes in an infinite electrolyte. These have recently been discussed.¹⁵ In the case of cylindrical electrodes, calculations have indicated that for relatively large diameters, greater than one inch, the plane-plate solution is applicable.¹⁶ When laminar or streamlined flow conditions prevail, experimental data in aqueous solution are in excellent agreement with theoretical predictions. Experimental data available are insufficient to justify this statement for turbulent flow conditions. The theoretical expressions for the average limiting current density and for the mass-transfer overpotential at current densities well below the limiting value are as follows:

$$i_{lim,av} = \frac{0.665nFD}{1-t} \cdot \frac{|c_e - c_b|}{h} (Gr_h Sc)^{\frac{1}{4}}; \quad (4)$$

and

$$\eta_{mt} = \frac{RT}{nF} \ln \frac{c_e}{c_b} = \frac{RT}{nF} \ln \left[1 \pm \frac{1.6i(1-t)}{nFD} \cdot \frac{y}{c_b} (Gr_y^* \cdot Sc)^{-\frac{1}{5}} \right]. \quad (5)$$

The negative part of the $\pm$ sign in Eq. (5) refers to cases where $c_e > c_b$, and vice versa. The dimensionless groups are defined as follows:

$$\text{The Schmidt number:} \quad Sc = \frac{\nu}{D}; \quad (6)$$

$$\text{The local Grashof number:} \quad Gr_y = \frac{g\alpha |c_e - c_b| y^3}{\nu^2}; \quad (7a)$$

$$\text{The maximum Grashof number:} \quad Gr_{lh} = \frac{g\alpha |c_e - c_b| h^3}{\nu^2}; \quad (7b)$$

$$\text{The modified local Grashof number:} \quad Gr_y^* = \frac{g\alpha i(1-t) y^4}{nFD\nu^2}. \quad (8)$$

The transition from laminar to turbulent natural flow occurs when

$$Gr_y \cdot Sc \approx 10^{11}.$$

In reasonably concentrated aqueous solutions, viz, 1-2 M,

$$y_{\text{trans}} \approx 5 \text{ cm.}$$

In any experimental electrode kinetic investigation, one should employ electrodes whose height is of this order of magnitude.

VII. CHARGE-TRANSFER OVERPOTENTIAL

Butler¹⁷ gave the first kinetic interpretation of electrode phenomena when he deduced the Nernst equation by applying statistical mechanics to ionic processes occurring at an electrode. Parsons,¹⁸ employing the theory of absolute reaction rates, has given the most general theory of charge-transfer polarization.

It is relevant at this point to consider the modern concept of the electrode-electrolyte interface. The theories of the electrochemical double layer have been detailed by Grahame¹⁹ and Parsons.^{20,21} A precise, lucid review of the present state of the theory is given by Mott and Watts-Tobin.²² The region contiguous with the interface may be considered as consisting of two sections. There is an inner layer, of the order of two molecular diameters in thickness. Here, there may be adsorbed ions, held partly by coulombic, and partly by specific, adsorption forces. Separating the inner layer from the bulk solution, where the charge distribution is random, is a transition zone, the Gouy-Chapman diffuse layer.²⁰ Here, a certain measure of charge orientation exists, which is attributed to a nonspecific coulombic interaction between the ionic charges in solution and the bound charges, i.e., those on the electrode surface and those held in the force field existing across the inner layer. The boundary between the inner and diffuse layers is called the "outer Helmholtz plane." The inner layer is itself divided into two regions by the "inner Helmholtz plane." The centers of specifically adsorbed ions are considered to lie in this plane. Before the charge-transfer process can occur, the reactants must be in the "pre-electrode layer" which is considered to be in the vicinity of the outer Helmholtz plane. The highest potential-energy barrier is considered to lie between the inner and outer Helmholtz planes.

The specific rate constant of any reaction is given by the familiar expression,

$$k_s = \frac{kT}{h} \exp(\Delta G^\# / RT), \quad (9)$$

where k and h are the Boltzmann and Planck constants, respectively. The superscript # refers to the activated state at the peak of the potential energy barrier. When one deals with physicochemical systems involving

charged particles, the chemical potential, μ , must be replaced by the electrochemical potential, $\bar{\mu}$, where

$$\bar{\mu} = \mu + zF\phi, \quad (10)$$

and ϕ is the "inner potential" of the phase in which the particle resides.²⁰ The inner potential difference between two phases is known as the "galvani potential difference." Let the inner potentials of the three phases, electrode, pre-electrode layer, and bulk solution be ϕ^M , ϕ^P , and ϕ^{soln} , respectively.

Consider now the general electrode charge-transfer reaction involving an oxidized species, O, and a reduced species, R. Let n electrons be involved in the overall transfer. Then,

Referring to the potential-energy diagram (Fig. 1), I and F indicate the initial and final states of the system; P_O and P_R are the pre-electrode states for the reactant and product species, O and R. The solid lines refer to the reaction at the equilibrium potential, E_e ; the broken lines refer to the reaction at the working potential, E . On the assumption that all states between the initial (final) and pre-electrode states are in equilibrium, the general relationship for the concentration of any species in the pre-electrode layer is

$$c^* = c_e \exp(-zF\Delta\phi^P/RT), \quad (12)$$

where c_e is the concentration at the electrode-electrolyte interface, just before the pre-electrode layer, and $\Delta\phi^P = \phi^P - \phi^{\text{soln}}$. If, by some external

Fig. 1. Energy Diagram for Kinetic Considerations

means, a potential difference, $E = \phi^M - \phi^{\text{soln}}$, is applied across the electrode-electrolyte interface, the free energy difference between I and F is changed by nFE . If the energy curves are assumed not to alter their shape or relative position along the reaction coordinate, then the change in energy of the activated state, A, can be said to be a linear function of $(E - \Delta\phi^P)$. Let us assume that generally the rate-determining step occurs ν times for each overall reaction, where ν is referred to as the stoichiometric number.^{3,23-26} The change in free energy of the activated state is then given by $\beta(n/\nu) \cdot (E - \Delta\phi^P)$, where the proportionality factor, β , the so-called symmetry factor, is given by

$$\beta = \frac{\tan \theta_{p_O}}{\tan \theta_{p_O} + \tan \theta_{p_R}} \quad (13)$$

The quantity (n/ν) is called the electron number, λ , and the product $\beta\lambda$ is the transfer coefficient, α . Let p' and q'' be the reaction orders for the retarded forward process; p'' and q' , for the facilitated backward process. The rates are given by

$$\vec{i} = \lambda F \frac{kT}{h} c_O^{*p'}/\nu c_R^{*q''}/\nu \exp\left[\frac{-\vec{\Delta}G_e^\# - \beta\lambda F(E - \Delta\phi^P)}{RT}\right] \quad (14a)$$

and

$$\overleftarrow{i} = \lambda F \frac{kT}{h} c_O^{*p''}/\nu c_R^{*q'}/\nu \exp\left[\frac{-\overleftarrow{\Delta}G_e^\# + (1 - \beta)\lambda F(E - \Delta\phi^P)}{RT}\right] \quad (14b)$$

Let

$$\vec{k}_e = \frac{kT}{h} \exp(-\vec{\Delta}G_e^\#/RT), \quad (15a)$$

and

$$\overleftarrow{k}_e = \frac{kT}{h} \exp(-\overleftarrow{\Delta}G_e^\#/RT). \quad (15b)$$

At equilibrium,

$$\vec{i} = \overleftarrow{i} = i_A^\circ,$$

where i_A° is called the apparent exchange current density. From Eqs. (12), (14), and (15), we obtain

$$i_A^\circ = \lambda F \vec{k}_e c_O^{p''/\nu} c_R^{q''/\nu} \exp[-\beta \lambda F (E_e - \Delta \phi_e^P) / RT] \exp[-(p' z_O + q'' z_R) F \Delta \phi_e^P / \nu RT]; \quad (16a)$$

and

$$i_A^\circ = \lambda F \vec{k}_e c_O^{p''/\nu} c_R^{q''/\nu} \exp[(1 - \beta) \lambda F (E_e - \Delta \phi_e^P) / RT] \exp[-(p'' z_O + q' z_R) F \Delta \phi_e^P / \nu RT]. \quad (16b)$$

At equilibrium, there is no net mass transfer, and the Nernst equation applies; viz,

$$E_e = E_e^\circ + \frac{RT}{nF} \ln \left[\frac{c_{O_b}^P}{c_{R_b}^q} \right]. \quad (17)$$

In this case,

$$c_O = c_{O_b}, c_R = c_{R_b}.$$

Equation (16a) may be written as

$$i_A^\circ = \lambda F \vec{k}_e c_{O_b}^{p'/\nu} c_{R_b}^{q''/\nu} \exp[-\beta \lambda F (E_e - E_e^\circ) / RT] \exp[-\beta \lambda F E_e^\circ / RT] \cdot \exp[\beta \lambda F \Delta \phi_e^P / RT] \exp[-(p' z_O + q'' z_R) F \Delta \phi_e^P / \nu RT]. \quad (18)$$

We define the standard rate constant, k° , as

$$k^\circ = \vec{k}_e \exp[-\beta \lambda F E_e^\circ / RT] = \vec{k}_e \exp[(1 - \beta) \lambda F E_e^\circ / RT]. \quad (19)$$

From Eq. (17), it is easy to obtain

$$\exp[-\beta \lambda F (E_e - E_e^\circ) / RT] = c_{O_b}^{-p\beta/\nu} / c_{R_b}^{-q\beta/\nu}; \quad (20a)$$

and

$$\exp[(1 - \beta) \lambda F (E_e - E_e^\circ) / RT] = c_{O_b}^{p(1-\beta)/\nu} / c_{R_b}^{q(1-\beta)/\nu}. \quad (20b)$$

Combination of Eqs. (18), (19), and (20) yields the expression

$$i_A^\circ = \lambda F k^\circ c_{O_b}^{(p' - \beta p)/\nu} c_{R_b}^{(q'' + \beta q)/\nu} \exp \left\{ \frac{[\beta n - (p' z_O + q'' z_R)] F \Delta \phi_e^P}{\nu R T} \right\}, \quad (21)$$

which may be written as

$$i_A^\circ = i^\circ \exp \left\{ \frac{[\beta n - (p' z_O + q'' z_R)] F \Delta \phi_e^P}{\nu R T} \right\}, \quad (22)$$

where i° is called the exchange current density and is given by

$$i^\circ = \lambda F k^\circ c_{O_b}^{(p' - \beta p)/\nu} c_{R_b}^{(q'' + \beta q)/\nu}. \quad (23)$$

We define the apparent standard rate constant, k_A° , as

$$k_A^\circ = k^\circ \exp \left\{ \frac{[\beta n - (p' z_O + q'' z_R)] F \Delta \phi_e^P}{\nu R T} \right\}. \quad (24)$$

When E and $\Delta \phi^P$ depart from their equilibrium values, the net forward rate is given as the difference of Eqs. (14a) and (14b); i.e.,

$$i = \vec{i} - \overleftarrow{i} = \lambda F \vec{k}_e c_O^{*p'/\nu} c_R^{*q''/\nu} \exp[-\beta \lambda F (E - \Delta \phi^P)/RT] - \lambda F \overleftarrow{k}_e c_O^{*p''/\nu} c_R^{*q'/\nu} \exp[(1 - \beta) \lambda F (E - \Delta \phi^P)/RT]. \quad (25)$$

The first part of Eq. (25) may be written as

$$\begin{aligned} & \lambda F \vec{k}_e c_O^{p'/\nu} c_R^{q''/\nu} \exp \left[\frac{-\beta \lambda F (E - E_e)}{RT} \right] \exp \left[\frac{-\beta \lambda F (E_e - E_e^\circ)}{RT} \right] \exp \left[\frac{-\beta \lambda F E_e^\circ}{RT} \right] \\ & \cdot \exp \left[\frac{\beta \lambda F \Delta \phi^P}{RT} \right] \exp \left[\frac{-(p' z_O + q'' z_R) F \Delta \phi^P}{\nu R T} \right] \exp \left\{ \frac{[-\beta n + (p' z_O + q'' z_R)] F \Delta \phi_e^P}{RT} \right\} \\ & \cdot \exp \left\{ \frac{[\beta n - (p' z_O + q'' z_R)] F \Delta \phi_e^P}{\nu R T} \right\}. \end{aligned} \quad (26)$$

Now

$$c_O^{p'/\nu} c_R^{q''/\nu} = c_{O_b}^{p'/\nu} c_{R_b}^{q''/\nu} (c_O/c_{O_b})^{p'/\nu} (c_R/c_{R_b})^{q''/\nu}; \quad (27a)$$

and

$$c_O^{p'/\nu} c_R^{q''/\nu} = c_{O_b}^{p''/\nu} c_{R_b}^{q'/\nu} (c_O/c_{O_b})^{p''/\nu} (c_R/c_{R_b})^{q'/\nu}. \quad (27b)$$

Combination of Eqs. (19), (20a), (22), and (27a), with (26) yields

$$i_A^{\circ} (c_O/c_{O_b})^{p'/\nu} (c_R/c_{R_b})^{q''/\nu} \exp[-\beta \lambda \eta_{ct} F/RT] \cdot \exp \left\{ \frac{[\beta n - (p' z_O + q'' z_R)] [\Delta \phi^P - \Delta \phi_e^P] F}{\nu RT} \right\}. \quad (28)$$

A similar expression holds for the second part of Eq. (25). The quantity η_{ct} is the charge-transfer overpotential. If $\eta_{ct} \leq$ approximately 5 mV, then $\Delta \phi^P \approx \Delta \phi_e^P$. Therefore, neglecting the second exponential factor in Eq. (28), we arrive at the relationship

$$i = i_A^{\circ} \left\{ (c_O/c_{O_b})^{p'/\nu} (c_R/c_{R_b})^{q''/\nu} \exp[-\beta \lambda \eta_{ct} F/RT] - (c_O/c_{O_b})^{p''/\nu} (c_R/c_{R_b})^{q'/\nu} \exp[(1 - \beta) \lambda \eta_{ct} F/RT] \right\}. \quad (29)$$

When charge-transfer polarization far exceeds mass-transfer polarization, $c_O = c_{O_b}$, and $c_R = c_{R_b}$. Therefore, we now have the familiar relationship

$$i = i_A^{\circ} \{ \exp[-\beta \lambda \eta_{ct} F/RT] - \exp[(1 - \beta) \lambda \eta_{ct} F/RT] \}. \quad (30)$$

From Eqs. (22), (23), and (24), the apparent standard rate constant for the charge-transfer reaction is given by

$$k_A^{\circ} = \frac{i_A^{\circ}}{\lambda F} \frac{(\beta p - p') \lambda / n}{c_{O_b}} \frac{-(\beta q + q'') \lambda / n}{c_{R_b}}. \quad (31)$$

If the reaction (11) is studied in the presence of an excess of supporting electrolyte, then except for extremely fast reactions, the effect of the electrochemical double layer may be neglected. Hence, i_A° and k_A° may be replaced by i° and k° , the real exchange current density and the standard rate constant, respectively.

At this point, it is relevant to consider the relationship between the various inner potentials, the measurable potential difference across the potentiometer binding posts, and the free energy change corresponding to the cell reaction. To explain this in a lucid manner, we will consider the galvanic cell in which the compound AX is produced spontaneously from the

elements A and X. For simplicity, let us assume that the overall charge transfer involves one electron. It is not necessary to consider the presence of a supporting electrolyte, nor to specify the solvent. We represent the cell as follows:

Here, M_1 and M_4 are the electrical leads to the potentiometer binding posts, and M_2 and M_3 are the metal supporting media for the electrode materials. Thus, for example, if A is molten alkali metal, the most suitable choice for M_2 is a porous matrix of compressed stainless-steel fiber. If X is a gas, then M_3 may be an inert, metallic, permeable diaphragm. At equilibrium, the following reversible transfers occur:

Phase Boundary	Reversible Transfer	Change in $\bar{\mu}$ or μ
M_1/M_2	$e^-(M_2) \rightleftharpoons e^-(M_1)$	$\bar{\mu}_{e^-}^{M_1} - \bar{\mu}_{e^-}^{M_2}$
M_2/A	$e^-(A) \rightleftharpoons e^-(M_2)$	$\bar{\mu}_{e^-}^{M_2} - \bar{\mu}_{e^-}^A$
$A/A^+(\text{soln})$	$A \rightleftharpoons A^+(\text{soln}) + e^-$	$\bar{\mu}_{A^+}^{\text{soln}} + \bar{\mu}_{e^-}^A - \mu_A$
$X^-(\text{soln})/X$	$X - e^- \rightleftharpoons X^-(\text{soln})$	$\bar{\mu}_{X^-}^{\text{soln}} - \mu_X - \bar{\mu}_{e^-}^X$
X/M_3	$e^-(M_3) \rightleftharpoons e^-(X)$	$\bar{\mu}_{e^-}^X - \bar{\mu}_{e^-}^{M_3}$
M_3/M_4	$e^-(M_4) \rightleftharpoons e^-(M_3)$	$\bar{\mu}_{e^-}^{M_3} - \bar{\mu}_{e^-}^{M_4}$

Utilizing Eq. (10) with $z = \pm 1$, we have, by summation from M_1 to M_4 ,

$$\mu_{A^+}^{\text{soln}} - \mu_A + \bar{\mu}_{X^-}^{\text{soln}} - \mu_X + \bar{\mu}_{e^-}^{M_1} - \bar{\mu}_{e^-}^{M_4} + F \left[\left(\phi_e^{M_1} - \phi^{\text{soln}} \right) - \left(\phi_e^{M_4} - \phi^{\text{soln}} \right) \right] = 0. \quad (32)$$

If M_1 and M_4 are made of the same material, then

$$\Delta G_e = F \left(\phi_e^{M_1} - \phi_e^{M_4} \right). \quad (33)$$

VIII. DETERMINATION OF CHARGE-TRANSFER KINETIC PARAMETERS, i_A° , k_A° , β , and λ

Considering the basic equation relating current density and the charge-transfer overpotential, (30), one can distinguish three main cases.

Case 1. For low values of η_{ct} , the exponentials may be expanded, second and higher powers being neglected; i.e.,

$$\eta_{ct} = \frac{RT}{\lambda F i_A^\circ} i = R_{ct} \cdot i. \quad (34)$$

The quantity $R_{ct} = RT/(\lambda F i_A^\circ)$ is called the charge-transfer resistance.²⁷

Case 2. For intermediate values of η_{ct} , full Eq. (30) must be used.

Case 3. For large values of η_{ct} , the first exponential factor in Eq. (30) may be neglected, and we have

$$\eta_{ct} = \frac{2.303RT}{(1-\beta)\lambda F} \log_{10} (i/i_A^\circ). \quad (35)$$

Equation (35) is referred to as the Tafel equation.²⁸

Plots of $|\eta_{ct}|$ versus i or $|\eta_{ct}|$ versus $\log_{10} i$ are referred to as polarization curves. A typical example (Elder and Hickling²⁹) is shown in Fig. 2. The apparent exchange current density i_A° may be obtained from the charge-transfer resistance, i.e., the slope of the curve for $|\eta_{ct}| - \log_{10} i$ at low $|\eta_{ct}|$, provided that λ is known. If the value of λ is unknown, it may be evaluated by considering the intermediate polarization region. Equation (30) may be re-written as

Fig. 2. Typical Overpotential Diagram (Reproduced from Elder and Hickling²⁹ by permission of the Faraday Society)

$$|\eta_{ct}| = \frac{2.303RT}{(1-\beta)\lambda F} \left\{ \log_{10} i - \log_{10} [1 - \exp(-\eta_{ct}\lambda F/RT)] \right\} - \frac{2.303RT}{(1-\beta)\lambda F} \log_{10} i_A^\circ \quad (36)$$

A plot of $|\eta_{ct}|$ versus

$$\log_{10} i - \log_{10} [1 - \exp(-\eta_{ct}\lambda F/RT)]$$

yields a straight line only if the correct value of λ is chosen. A typical example (Elder and Hickling²⁹) is shown in Fig. 3. From the slope and intercept on either axis, β and i_A° may be obtained. Analysis of the linear Tafel plot (upper portion of curve, Fig. 2) enables one to check these values. Reaction orders can be

evaluated by investigating the variation of i_A° with the concentration of the species O and R. Thus, neglecting the double-layer correcting factor in Eq. (21), we have

$$\left(\frac{\partial \ln i_A^\circ}{\partial \ln c_{O_b}} \right)_{c_{R_b}} = \frac{p' - \beta p}{\nu}; \quad (37a)$$

$$\left(\frac{\partial \ln i_A^\circ}{\partial \ln c_{R_b}} \right)_{c_{O_b}} = \frac{q'' + \beta q}{\nu}. \quad (37b)$$

Fig. 3
Modified Overpotential Diagram (Reproduced
from Elder and Hickling²⁹ by permission of
the Faraday Society)

IX. THEORY OF THE TECHNIQUES FOR INVESTIGATING ELECTRODE KINETICS

A. Voltammetry

Voltammetry is the conventional method for studying the relationship between current density and electrode potential, utilizing either macro-electrodes of superficial surface area in the range 1-10 cm², or micro-electrodes in the range $5 \cdot 10^{-5}$ - $5 \cdot 10^{-3}$ cm². Voltammetry may be carried out under conditions of either controlled potential or controlled current.

1. Controlled-potential Electrolysis

Essentially there are three primary techniques utilizing potential control for the investigation of the kinetics of electrochemical processes. One may execute voltammetric studies at constant, continuously-varying, and periodically-varying potentials. As the name implies, voltammetry with periodically-varying potential is essentially an a.c. method and will be discussed as such (see Sect. IX-C).

a. Constant-potential Voltammetry

Constant-potential voltammetry embraces all techniques whereby, between individual settings of the working-electrode potential with respect to an arbitrarily chosen reference, the system attains a steady state as regards mass- and charge-transfer processes. Thus, one may include the important techniques of conventional (dropping mercury electrode, DME) and solid microelectrode polarography.

At this point, it is relevant to consider the basic mode of operation of an apparatus for controlled-potential electrolysis. Hickling³⁰ coined the term potentiostat for such an instrument. The fundamental circuit for potentiostatic control is shown in Fig. 4A. The electrolyzing current from a stable d.c. source passes through the tube V. Initially, the current is so controlled that the potential drop across the working-reference electrode system is the desired value. Any drift in this potential drop is impressed as an error signal on the amplifier circuit. The amplified signal changes the grid bias of V so as to vary the electrolysis current and nullify the error signal. Lingane³¹ has given a detailed account of the development of

Fig. 4. Basic Potentiostatic and Galvanostatic Circuits

modern potentiostat design. For each potential setting, the current and, hence, current density (based upon superficial area) are measured. The

Fig. 5 Hypothetical Polarization Curves

shape and position of the polarization curves (i versus E_i) indicate the various electrochemical reactions that occur. Figure 5 shows two types of polarization curves. Curve 1 indicates a reaction involving a rapid charge-transfer process, i.e., little polarization over a wide current-density range. At point A, mass-transfer phenomena start to exert an effect. Finally, a limiting current-density plateau is observed. If no other electrode process can proceed, then i will never exceed $i_{lim,1}$. In Curve 2, at relatively low current densities, there is large polarization, indicative of a slow charge transfer. Again, at a point B, mass-

transfer effects are in evidence, culminating in a limiting current. If a second electrode process is capable of being sustained while the first is proceeding at its limiting rate, $i_{lim,2}$, then with further increase in E_i , i increases, eventually attaining a limiting value, $i_{lim,3}$ (Curve 3). Ultimately, an electrode process will occur, which involves the breakdown of the solvent medium.

Conventional polarography, utilizing the DME, has been discussed by Lingane,³¹ Kolthoff and Lingane,³² Delahay,³³ and Meites.³⁴ In this technique, the potential is applied in incremental steps and is not a linear-sweep method. The rate of change of potential is usually sufficiently slow for attainment of steady-state conditions at every potential setting. The use of a microelectrode obviates the need for a third reference electrode. The magnitude of the cell current is so small that the ohmic drop is insignificant, and the relatively large second working electrode remains essentially unpolarized and, hence, serves a dual role, that of counter-and-reference electrode.

b. Continuously-varying-potential Voltammetry

The two basic techniques for voltammetry with a continuously-varying potential are the single- and multisweep methods.

(1) The Single-sweep Method

As for constant-potential voltammetry, the two-electrode cell (microelectrode and large counter-reference electrode) is used. If a condenser is charged galvanostatically from a high-voltage power

supply, a voltage varying linearly with time may be generated. If v_c is the output of the power supply and RC is the time constant of the circuit, then the rate of potential change, dV/dt , is given by v_c/RC . The potential of the indicator electrode (working microelectrode) at any time, t , is

$$E_t = E_e \pm \frac{v_c}{RC} t \mp R_c(I_f + I_{dl}), \quad (38)$$

where upper signs refer to increasing anodic potentials, the lower signs to increasing cathodic potentials, R_c is the cell resistance and I_f and I_{dl} are the faradaic current (electrochemical reaction) and capacity current (electrochemical double-layer charging), respectively. The boundary-value problems for both linear and cylindric diffusion have been discussed by Delahay.³³ Theoretical current-potential relationships have been derived and experimentally verified for certain specific problems. These relationships are characterized by peaks, instead of plateau regions as in constant-potential voltammetry. The peak faradaic current is directly proportional to the square root of the rate of potential change and to the concentration of electroactive species. As seen from Eq. (38), the theoretical current-potential curves and the theoretical peak faradaic current, which are derived on the assumption that the ohmic factor in this equation may be neglected, are distorted by these factors. Experimental methods for compensating these extraneous factors are discussed by Delahay.³³

Gilman,^{35,36} has employed a variation of the single-sweep technique, the multipulse potentiodynamic (MPPD) method, which has proved a useful technique in investigating adsorption phenomena and their effect on electrode kinetics.

(2) The Multisweep Method

In the multisweep method, current-potential curves are recorded oscillographically when the applied voltage is a periodic function of time. For example, both sawtooth and isosceles triangular voltage sweeps have been employed. Since the concentration distributions of electroactive species in the region contiguous with the indicator electrode after each sweep are not necessarily the same, the current-potential curves so obtained are not superimposable. The boundary-value problems associated with these varying conditions are difficult to set up and well-nigh impossible to solve. The term cyclic voltammetry is applied to the specific type of multisweep method involving linear-sweep voltammetry with repeated current reversal.³⁷ These multisweep techniques have been employed in analytical chemistry and in studying electrochemical double-layer phenomena. Their use as a tool in the investigation of electrode kinetics has been supplanted by the more powerful perturbation-relaxation methods which will be discussed in Sect. B below.

2. Controlled-current Electrolysis

Whereas electrochemical studies under potentiostatic control are eminently suitable for investigating the polarization characteristics of a system over a wide range of potentials, the detailed investigation of such characteristics over smaller ranges of potential is best carried out under galvanostatic control. The simple galvanostatic circuit is shown in Fig. 4B. From the more precise potentiometric data, a plot of η_{ct} versus $\log i$ is set up and analyzed as indicated in Sect. VIII. The experimental curve shown in Fig. 2 was evaluated from data obtained under galvanostatic control.²⁹

The kinetic parameters, β , λ , and i_A° , descriptive of charge-transfer processes, can only be determined by means of conventional potentiostatic or galvanostatic voltammetry if $k_A^\circ \leq 10^{-2}$ cm/sec. For more rapid electrode reactions, more sophisticated techniques must be used.

B. Perturbation-Relaxation Techniques

1. Introduction

The perturbation-relaxation methods involve the application of voltage or current pulses, usually in the form of a rectangular step function, to the system under investigation. The resulting current or potential-time transient is then monitored, usually oscillographically. The actual electrolysis time is of such short duration that any contribution to mass transfer due to convection is negligibly small. However, diffusion cannot be discounted and must be considered in setting up relationships involving either E_i or i as a function of time. With reference to the general system (11), because of the complexities in the mathematical treatments, the only case which can be treated theoretically is when $p = p' = q = q' = \nu = 1$. Since $p'' = p' - p$, and $q'' = q' - q$, it follows that $p'' = q'' = 0$. Therefore, $\lambda = n$, and $\beta = \alpha$. When η_{ct} is small, the concentration ratios in Eq. (29) are not too far removed from unity, and this equation may be linearized by expanding and considering only the first two terms of the expansion. Thus, the starting points for any theoretical analysis are either of the following equations:

$$i = i_A^\circ \left\{ \left(\frac{c_O}{c_{Ob}} \right) \exp \left[\frac{-\alpha n \eta_{ct} F}{RT} \right] - \left(\frac{c_R}{c_{Rb}} \right) \exp \left[\frac{(1 - \alpha) n \eta_{ct} F}{RT} \right] \right\}; \quad (39a)$$

and

$$i_{\eta_{ct} \rightarrow 0} = i_A^\circ \left\{ \left(\frac{c_O}{c_{Ob}} \right) - \left(\frac{c_R}{c_{Rb}} \right) - \frac{n \eta_{ct} F}{RT} \right\}. \quad (39b)$$

Current-time or potential-time variations may be derived if mass transfer is assumed to be controlled by semi-infinite linear diffusion; i.e., the cell dimensions are so large, in comparison with the dimensions of the plane-plate electrode, that the electrolyte may be considered as extending to infinity.

In dealing with any mass-transfer problem, one must set down the initial and boundary conditions relevant to the problem at hand in order that the diffusion equations³⁸ may be solved. For the species O, one has the relationships for the molar flux

$$q_O(x, t) = D_O \cdot \frac{\partial}{\partial x} [c_O(x, t)], \quad (40a)$$

and for the rate of change of concentration,

$$\frac{\partial}{\partial t} [c_O(x, t)] = D_O \frac{\partial^2}{\partial x^2} [c_O(x, t)], \quad (40b)$$

and analogous expressions relating to the reduced species, R.

Initial conditions:

$$c_O(x, 0) = c_{O_b}; \quad (41a)$$

$$c_R(x, 0) = c_{R_b}. \quad (41b)$$

Boundary conditions:

$$i = nFq_O(0, t) = -nFq_R(0, t); \quad (42)$$

$$c_O(x \rightarrow \infty, t) \rightarrow c_{O_b}, \quad (43a)$$

$$c_R(x \rightarrow \infty, t) \rightarrow c_{R_b}; \quad (43b)$$

$$q_O(0, t) + q_R(0, t) = 0. \quad (44)$$

For simplicity, let

$$f_1 = \frac{-\alpha n \eta_{ct} F}{RT}, \quad f_2 = \frac{(1 - \alpha) n \eta_{ct} F}{RT}.$$

2. Potentiostatic Methods

In potentiostatic methods, the potential difference across (a) the working-reference electrode couple and (b) the two working electrodes, one of which must be unpolarizable, is suddenly changed from its equilibrium or open-circuit value by means of an externally-applied voltage-step function. The resulting current-time transient is followed oscillographically. The two methods for cases (a) and (b) are termed, respectively, (a) the potential-step method, and (b) the voltage-step method. The advantage of the latter method concerns the experimental technique in that there is no necessity for the use of a Luggin-Haber capillary. The disadvantages are the necessity of having one unpolarizable working electrode and the necessity of restricting the voltage-step function to 2-5 mV, so that the mathematical analysis may be applicable. The Laplace transformation technique is utilized in the manner outlined by Delahay³⁹ to establish expressions relating c_O/c_{O_b} and c_R/c_{R_b} as functions of time.

a. Potential-step Method

The theory of the potential-step method was first given by Gerischer and Vielstich.^{40,41} As their derivation is only given in outline for a slightly different overall process and furthermore contains a typographical error, it is repeated here and is shown as a simple example of the application of the Laplace transformation technique^{42,43} to this type of problem. Consideration of the boundary condition (42) indicates that the important parameters to be obtained by solving the second-law diffusion Eq. (40b) are $q_O(0, t)$ and $q_R(0, t)$. For simplicity, the parameters λ_O , λ_R , and χ are introduced, where

$$\lambda_O = \frac{i_A^0 \exp f_1}{nFc_{O_b}D_O}, \quad (45a)$$

$$\lambda_R = \frac{i_A^0 \exp f_2}{nFc_{R_b}D_R}, \quad (45b)$$

and

$$\chi = \frac{D_R}{D_O}. \quad (46)$$

Let $c_O(x, s)$ and $c_R(x, s)$ be the Laplace transforms of $c_O(x, t)$ and $c_R(x, t)$; i.e.,

$$c_O(x, s) = \int_0^\infty e^{-st} c_O(x, t) dt; \quad (47a)$$

and

$$c_R(x, s) = \int_0^{\infty} e^{-st} c_R(x, t) dt. \quad (47b)$$

Then Eq. (40b) and its analog for the reduced species, R, are

$$s c_O(x, s) - c_{O_b} = D_O c_O''(x, s); \quad (48a)$$

and

$$s c_R(x, s) - c_{R_b} = D_R c_R''(x, s). \quad (48b)$$

The Laplace-transformed boundary conditions (42) and (43) are

$$-i/(nFD_O s) = c_O'(0, s) = \lambda_O c_O(0, s) - \chi \lambda_R c_R(0, s), \quad (49a)$$

and

$$-i/(nFDR s) = c_R'(0, s) = \lambda_R c_R(0, s) - \frac{\lambda_O}{\chi} c_O(0, s); \quad (49b)$$

where the single primes refer to differentiation with respect to x , and

$$c_O(\infty, s) = c_{O_b}/s, \quad (50a)$$

and

$$c_R(\infty, s) = c_{R_b}/s. \quad (50b)$$

Let

$$c_O(x, s) = F(s) \exp(-k_1 x) + c_O(\infty, s), \quad (51a)$$

and

$$c_R(x, s) = G(s) \exp(-k_2 x) + c_R(\infty, s). \quad (51b)$$

Insertion of Eqs. (51) and their second derivatives with respect to x , at $x = 0$, into Eqs. (48) yields

$$k_1 = (s/D_O)^{1/2},$$

$$k_2 = (s/D_R)^{1/2},$$

$$F(s) = \psi s^{-1} [\phi_1 + s^{1/2}]^{-1},$$

and

$$G(s) = -\chi^{-1/2} F(s),$$

where the parameters ψ and ϕ_1 are given by

$$\psi = \chi^{1/2} \lambda_R D_R^{1/2} c_{R_b} - \lambda_O D_O^{1/2} c_{O_b}; \quad (52)$$

and

$$\phi_1 = \lambda_O D_O^{1/2} + \lambda_R D_R^{1/2}. \quad (53)$$

Hence,

$$c_O(0, s) = \frac{-\psi}{s^{1/2} D_O^{1/2} (\phi_1 + s^{1/2})}; \quad (54a)$$

and

$$c_R(0, s) = \frac{\psi}{\chi s^{1/2} D_O^{1/2} (\phi_1 + s^{1/2})}. \quad (54b)$$

Taking the inverse transforms (Churchill,⁴³ p. 297, No. 43) results in

$$c_O(0, t) = \frac{x}{D_O^{1/2}} \exp(\phi_1^2 t) \operatorname{erfc}(\phi_1 t^{1/2}); \quad (55a)$$

and

$$c_R(0, t) = \frac{\psi}{\chi \cdot D_O^{1/2}} \exp(\phi_1^2 t) \operatorname{erfc}(\phi_1 t^{1/2}). \quad (55b)$$

Hence, from Eqs. (40a), (42), and (55),

$$i = i_A^0 \exp \left\{ \left[\frac{-\alpha n \eta_{ct} F}{RT} \right] - \exp \left[\frac{(1 - \alpha) n \eta_{ct} F}{RT} \right] \right\} \exp(\phi_1^2 t) \operatorname{erfc}(\phi_1 t^{1/2}), \quad (56)$$

where erfc is the complement of the error-function integral.⁴⁴ The function $\exp(x^2) \operatorname{erfc}(x)$, which is tabulated by Carslaw and Jaeger,⁴² gives a measure of the effect of diffusive mass-transfer polarization. For small and large

values of the argument x , this factor simplifies to $1 - 2x/\pi^{1/2}$ and $1/(\pi^{1/2}x)$, respectively. For small values of t , therefore, the linear plot of $i - t^{1/2}$ is made from experimental data for $i - t$ for varying values of the potential step function, from which η_{ct} may be easily calculated. By extrapolating to $t = 0$ (no mass-transfer polarization), the corrected data for $\eta_{ct} - i$ are obtained. The kinetic parameters are then evaluated by analyzing these polarization data as described in Sect. VIII.

b. Voltage-step Method

The theory of the voltage-step method has been given by Vielstich and Delahay.⁴⁵ Contrary to the theory of the potential-step method, a solution to the boundary problem under these experimental conditions can only be given if one employs the linearized kinetic Eq. (39b). This accounts for the restriction on the magnitude of the voltage pulse. In addition to the conditions (41)-(44), it is necessary to prescribe

$$\eta_{ct} = \Delta V + IR_t, \quad (57)$$

where R_t is the total cell and circuit resistance, and ΔV is the magnitude of the voltage pulse. The final theoretical relationship of current density and time is similar to Eq. (56); i.e.,

$$i = \left(\frac{\Delta V}{R_t + R_{ct}} \right) \exp(\phi_2^2 t) \operatorname{erfc}(\phi_2 t^{1/2}), \quad (58)$$

where R_{ct} is the charge-transfer resistance²⁷ (see Sect. VIII), and the function ϕ_2 is given by

$$\phi_2 = \left(\frac{1}{nFi_A^\circ} + \frac{1}{R_t R_{ct}} \right) \left(\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right). \quad (59)$$

Again, for small t , a plot of i as a function of $t^{1/2}$ is linear. The slope is the reciprocal of $(R_t + R_{ct})$. The intercept at $t = 0$ is $\Delta V[R_t + RT/(nFi_A^\circ)]$. Thus, the initial current is dependent upon both R_{ct} and R_t . For this method to give a measure of i_A° comparable in accuracy with that evaluated from potential-step data, the charge-transfer resistance should be very much greater than the cell and circuit resistance. The assumption that the kinetically-controlled current instantaneously rises to a maximum at the point at which the voltage pulse is applied is not valid. Electrochemical double-layer charging must be taken into account. During this charging time, the potential of the indicator electrode builds up from zero to the maximum value ΔV , according to the equation

$$\Delta V_t = \Delta V \left[1 - \exp\left(-\frac{t}{R_t c_{dl}}\right) \right], \quad (60)$$

where c_{dl} is the differential double-layer capacity.³³ During the first few microseconds, the charging current, given by

$$I_{dl} = \frac{\Delta V}{R_t} \exp\left(-\frac{t}{R_t c_{dl}}\right) \quad (61)$$

decreases and the faradaic current, I_f , increases to a maximum. Therefore, the intercept at $t = 0$ will yield a value of i_A^0 which is too large. Laitinen, Tischer, and Roe⁴⁶ have discussed this point in detail and have employed an empirical treatment of observed data to correct for finite double-layer charging.

3. Galvanostatic and Associated Methods

If a constant current is passed through a cell and the only resistance to flow of charge is the charge-transfer resistance,²⁷ then if the active surface area of the working electrode is unaffected by the electrode process (a condition that is never fulfilled in practice), the charge-transfer overpotential, η_{ct} , is independent of time (Fig. 6A). In actuality, at the start of

Fig. 6. Hypothetical Characteristics of Overpotential versus Time for a Galvanostatically-perturbed Electrochemical System

electrolysis, a certain fraction of the total current is required to charge the double layer. This fraction is given by $A c_{dl} d\eta/dt$, where A is the active electrode area. After a relatively short period of time (~ 1 msec), $d\eta/dt = 0$. The charging curve is as shown (Fig. 6B). If mass-transfer effects contribute to the observed overpotential, then $d\eta/dt$ never decreases to zero and the overpotential increases steadily with time (Fig. 6D). In the early stages of electrolysis, mass-transfer effects are due entirely to diffusion. In the later stages, however, both convection and diffusion, and in the absence of excess of a supporting electrolyte, migration must be considered in evaluating the total mass-transfer polarization.

Various theoretical analyses of the overpotential-time characteristics of electrochemical systems perturbed galvanostatically have been presented. In most cases, the analysis has assumed either mass- or charge-transfer control. Only recently has an analysis been given that takes into account double-layer charging, the kinetics of the charge-transfer process, and diffusive mass transfer.

a. Charging-current Methods

The galvanostatic charging-current method, originated by Bowden and Rideal,⁴⁷ has been used extensively by Hickling et al.,⁴⁸ Frumkin et al.,⁴⁹ and Butler et al.⁵⁰ (see also Elder⁵¹). For a more complete bibliography, see Breiter, Knorr, and Völkl,⁵² and Elder.⁵³

The total current density is given by the sum of the faradaic and capacitive components. The double-layer charging-current density is given by the following relationship:

$$i_{dl} = -c_{dl} \frac{d\eta_t}{dt} \quad (62)$$

The concentration ratios in Eq. (39a) approach unity, if mass-transfer effects are negligible. Hence, the basic differential equation describing the buildup of charge-transfer overpotential is

$$\frac{d\eta_t}{dt} = -\frac{1}{c_{dl}} \left\{ i_{tot} - i_A^0 \left[\exp\left(\frac{-\alpha n \eta_t F}{RT}\right) - \exp\left(\frac{(1-\alpha) n \eta_t F}{RT}\right) \right] \right\} \quad (63)$$

Roiter, Juza, and Polujan⁵⁴ have given a solution to this nonlinear differential equation for the specific case, $\alpha = 1/2$. Bockris and Potter⁵⁵ have given approximate solutions for certain specific values for the final charge-transfer overpotential, η_{ct} . Matsen⁵⁶ has solved the equation on an analog computer. His calculations have shown that marked variations in either α or i_A^0 have little effect on the shape of the evaluated charging curves. He concludes that the evaluation of the kinetic parameters from the analysis of a single charging curve could yield highly inaccurate values, but points to a more promising approach, viz, an analysis of the plot of the first derivative, $d\eta_t/dt$ as a function of η_t . The quantity c_{dl} may be evaluated from the extrapolated value of this derivative at $\eta_t = 0$. From Eq. (63), one has

$$\left[\frac{d(d\eta_t/dt)}{d\eta_t} \right]_{t=0} = \frac{-i_A^0 n F}{c_{dl} RT} \quad (64)$$

Hence, i_A^0 may be evaluated. Karasyk, Law, and Linford⁵⁷ have solved Eq. (63), modified by replacing the term $(1-\alpha)$ by $(\theta-\alpha)$, where $0 < \alpha \leq \theta \leq n$. This takes into account the fact that the sum of the anodic and cathodic transfer coefficients are not always equal to unity.⁵⁸ Several equations were developed involving η_t as logarithmic functions of the current density, differential double-layer capacity per unit area, and the kinetic parameters of the system. By means of these equations, a digital program involving a least-squares averaging process was written to obtain estimates of the kinetic parameters from a single charging curve.

b. Chronopotentiometry

The term chronopotentiometry was coined by Delahay and Mamantov⁵⁹ to describe potential-time studies of systems perturbed galvanostatically under conditions of linear diffusion control. The theory underlying this technique was very early developed by Weber,⁶⁰ Sand,⁶¹ and Roseburgh and Miller,⁶² who employed Fick's laws of diffusion³⁸ to express the concentration of the potential-determining species as a function of both time and distance, orthogonal to the electrode surface. For the simple redox system

the concentrations of the reactants, $c_O(x, t)$ and $c_R(x, t)$ are obtained by solving equations of the same type as Eq. (40b) with initial and boundary conditions (41)-(44). The mathematical treatment is similar to that outlined for the potential-step method in Par. IX-B-2-a above. The Laplace-transformed second-law diffusion equations are as previously given in Eqs. (48). For this problem, the transforms of the boundary conditions (42) are

$$c_O(0, s) = \frac{i}{nFD_O s}, \quad (66a)$$

and

$$c_R(0, s) = \frac{-1}{nFD_R s}. \quad (66b)$$

The transforms of boundary conditions (43) are as previously given in Eqs. (50). Again, $c_O(x, s)$ and $c_R(x, s)$ are given by the exponential relationships (51). Solution of these equations yields the following values for the several coefficients, $k_1 = (s/D_O)^{1/2}$, $k_2 = (s/D_R)^{1/2}$, $F(s) = -i(nFD_O^{1/2}s^{3/2})$, and $G(s) = i/(nFD_R^{1/2}s^{3/2})$. Therefore, incorporating these values, together with Eqs. (50a) and (50b), in Eqs. (51a) and (51b), one obtains

$$c_O(x, s) = \frac{c_{O_b}}{s} - \frac{i}{nFD_O^{1/2}} s^{-3/2} \exp\left[-\frac{s^{1/2}}{D_O^{1/2}} x\right]; \quad (67a)$$

and

$$c_R(x, s) = \frac{c_{R_b}}{s} + \frac{i}{nFD_R^{1/2}} s^{-3/2} \exp\left[-\frac{s^{1/2}}{D_R^{1/2}} x\right]. \quad (67b)$$

Taking the inverse transforms (Churchill,⁴³ pp. 295 et seq., Nos. 1 and 85) results in

$$c_O(x, t) = c_{O_b} - \frac{2i}{nF} \left(\frac{t}{\pi D_O} \right)^{1/2} \exp \left[-\frac{x^2}{4D_O t} \right] + \frac{ix}{nF D_O} \operatorname{erfc} \left[\frac{x}{2D_O^{1/2} t^{1/2}} \right]; \quad (68a)$$

and

$$c_R(x, t) = c_{R_b} + \frac{2i}{nF} \left(\frac{t}{\pi D_R} \right)^{1/2} \exp \left[-\frac{x^2}{4D_R t} \right] - \frac{ix}{nF D_R} \operatorname{erfc} \left[\frac{x}{2D_R^{1/2} t^{1/2}} \right]. \quad (68b)$$

Equations (68a) and (68b) representing the instantaneous concentrations of both species were first given by Karaoglanoff.⁶³ The instantaneous concentrations at the electrode surface are then of the form

$$c_O(0, t) = c_b + \frac{2it^{1/2}}{nF\pi^{1/2}D^{1/2}} \quad (69)$$

More complicated electrochemical systems may be treated in a similar manner, by setting up the appropriate boundary-value problems. Thus, the problems of consecutive electrochemical reactions involving different species,⁶⁵ stepwise electrode processes,^{65,66} cathodic reductions followed by anodic oxidations, and vice versa,⁶⁵ electrochemical processes preceded^{64,67} or succeeded⁶⁸ by slow chemical processes have been treated theoretically. For reversible electrode systems, equations of the same type as Eq. (69) are inserted into the Nernst Eq. (17), correctly written in terms of activities, yielding the appropriate potential-time relationship:

$$E_e = E_e^\circ + \frac{RT}{nF} \ln \left[\frac{\gamma_O D_R^{1/2}}{\gamma_R D_O^{1/2}} \right] + \frac{RT}{nF} \ln \left[\frac{nF\pi^{1/2}c_{O_b}D_O^{1/2} - 2it^{1/2}}{nF\pi^{1/2}c_{R_b}D_R^{1/2} + 2it^{1/2}} \right]. \quad (70)$$

An equation of this type was first derived by Karaoglanoff.⁶³ It may be shown³³ that the first two terms on the right-hand side of Eq. (70) comprise the half-wave potential, $E_{1/2}$, which is the characteristic potential at which the cell current attains one-half the limiting value, when the current-potential characteristics of the redox system are determined by means of the two-electrode voltammetric technique. When t attains a value τ , the transition time⁶⁹ defined by the relationship

$$\tau^{1/2} = \frac{nF\pi^{1/2}c_{O_b}D_O^{1/2}}{2i}, \quad (71)$$

the electrode potential E_e is theoretically infinite. In practice, at time τ , the electrode potential starts to change rapidly until a new reaction proceeds at

the electrode. In the absence of any other oxidant, solvent breakdown will occur. For the simple redox system (65) $i\tau^{1/2}$ is independent of i . If however, the concentration of the species, O, is dependent upon the kinetics of a preceding chemical process

then, as shown by Delahay and Berzins⁶⁴ and Gierst and Juliard,⁷⁰ a plot of $i\tau^{1/2}$ as a function of i may show a slow linear decrease, finally becoming constant as i increases. Under these conditions, a modified form of Eq. (71) is valid; viz,

$$\tau^{1/2} + \frac{\pi^{1/2} \text{erf}[(k_f + k_r)^{1/2} \tau^{1/2}]}{2K(k_f + k_r)^{1/2}} = \frac{nF\pi^{1/2} c_{O_b} D_O^{1/2}}{2i}, \quad (73)$$

where k_f and k_r are the specific rate constants for the forward and reverse directions of Eq. (72), and K is the equilibrium constant, k_f/k_r . If the argument of the error-function integral is greater than 2, then this integral takes the constant value, unity.⁴⁴ Therefore,

$$i\tau^{1/2} = \frac{nF\pi^{1/2} c_{O_b} D_O^{1/2}}{2} - \frac{i\tau^{1/2}}{2K(k_f + k_r)^{1/2}}. \quad (74)$$

Furthermore, if K is very large, the magnitude of the negative slope of plot of $i\tau^{1/2}$ versus i may be so small that the slow linear decrease may not be observable. On the other hand, if the argument of the error function integral is less than 0.1, one may expand this integral as a power series and take the first term; then in the limit, as the current density attains large values,

$$i\tau^{1/2} = \frac{K}{K + 1} \frac{nF\pi^{1/2} c_{O_b} D_O^{1/2}}{2}; \quad (75)$$

i.e., a plot of $i\tau^{1/2}$ versus i decreases with increase in i , ultimately attaining the constant value given by Eq. (75).

In contrast, if the electrochemical process is followed by a slow nonelectrochemical removal of the reduced species R,

then, as shown by Delahay, Mattax, and Berzins,⁶⁸ the transition time is still given by Eq. (71) and $i\tau^{1/2}$ is still independent of the current density. The only effect of the subsequent slow chemical reaction is a displacement of the potential-time curves, the magnitude of the displacement being dependent upon the relative values of k_f and k_r .

For a totally irreversible electrode process, the kinetics of the charge-transfer step must be taken into account. If one neglects the effect of the double layer and considers the necessary simplifications with regard to the orders of reaction and stoichiometric number stated at the beginning of this section, then from Eqs. (14) and (15) one obtains relationships of the type

$$i_C = nF\vec{k}_e c_O(0, t) \exp\left[\frac{-\alpha n E_i F}{RT}\right]; \quad (77a)$$

and

$$i_A = nF\vec{k}_e c_R(0, t) \exp\left[\frac{(1 - \alpha) n E_i F}{RT}\right]. \quad (77b)$$

The resulting potential-time relationships are obtained by combining equations of the same types as Eqs. (69) and (77).

Reinmuth has discussed potential-time and $i\tau^{1/2}$ relationships for various types of processes involving O-R redox systems in which no complications other than diffusive mass transfer precede the charge-transfer process⁷¹ and where the charge transfer is preceded by adsorption and/or slow chemical steps.⁶⁷ Testa and Reinmuth⁶⁶ have extended the original theoretical treatment of Berzins and Delahay⁶⁵ regarding step-wise electrochemical phenomena to take into account preceding, intermediate, and succeeding slow chemical steps. In all cases, diagnostic criteria are presented to distinguish the several kinetic schemes. A novel extension of the simple chronopotentiometric technique is discussed by Testa and Reinmuth;⁷² the normal constant-current technique is replaced by a current step-function. Expressions have been derived for the instantaneous electrode surface concentrations for the simple redox system (65) and for multicomponent systems. Herman and Bard⁷³ have recently introduced the technique of cyclic chronopotentiometry, in which the constant current is continually reversed at potentials taken at the transition times for the various processes. Using Duhamel's theorem,^{42,74} they have rigorously derived the Murray-Reilly⁷⁵ current-impulse response functions for linear diffusion and used them to derive equations for the current-concentration-transition time relationships.

c. Galvanostatic Pulse Methods

Berzins and Delahay^{76,77} proposed the use of a galvanostatic pulse technique as a method of studying the kinetics of rapid charge-transfer reactions. They have also given a detailed theoretical analysis of the method, taking into account double-layer charging, the charge-transfer step, and diffusive mass-transfer phenomena.⁷⁸

The potential of the working electrode, whose kinetics are being investigated, is adjusted at its equilibrium value and a single constant-current pulse, in the form of a rectangular step function, is passed between it and a counter working electrode. This counter electrode may be an unpolarized electrode or it may be identical with the first working electrode. However, in either case, the ratio of the area of the counter to that of the working electrode should be of the order 10^2 - 10^3 . The potential of the working electrode is monitored as a function of time oscillographically. As in the voltage-step method (see Par. IX-B-2-b above), because of mathematical complexities, one has to employ the relationship of linearized charge-transfer current density to potential, Eq. (39b). Thus, one is limited to employing current pulses of such magnitude that the potential excursion of the working electrode from its equilibrium value is of the order 0-5 mV. The initial and boundary conditions (41)-(44) are valid. For this particular boundary-value problem, in order to take into account the charging of the double layer, an extra boundary condition is required, viz,

$$i_{\text{tot}} = i_f + i_{dl} \quad (78)$$

where i_f is the faradaic component of the total current density, given by Eq. (39b), and i_{dl} is given by Eq. (62). The general relationship between $|\eta|$ and t may be written in the simple form⁷⁸

$$|\eta| = i_{\text{tot}} R_{ct} + \beta_1 (t^{1/2} - t^{*1/2}) \quad (79)$$

where R_{ct} is the charge-transfer resistance²⁷ [cf Eq. (34)] and the parameters β_1 and t^* are given by

$$\beta_1 = \frac{2i_{\text{tot}}RT}{\pi^{1/2}n^2F^2} \left[\frac{1}{c_{Ob}D_O^{1/2}} + \frac{1}{c_{Rb}D_R^{1/2}} \right] \quad (80)$$

and

$$t^{*1/2} = \frac{\pi c_{dl} \beta_1}{4i_{\text{tot}}} \quad (81)$$

Because of the limitation on the potential excursion, the ohmic drop across the cell will be much larger than the electrode potential changes, especially in the early stages of the electrolysis. One may compensate for this vitiating effect by including a bridge circuit in the current-pulse and potential-time recording circuit. This bridge may also be employed to measure the differential double-layer capacity which is necessary in order to evaluate the kinetic parameters from the slope and intercept of the linear plot of $|\eta| - t^{1/2}$.

A serious limitation of this method, especially when one is investigating exceedingly rapid electrode reactions, is that, in the initial period after application of the pulse, the current is primarily nonfaradaic, and the above theory is invalid in this region. With this point in mind, Gerischer and Krause^{79,80} developed the double-pulse galvanostatic method. A current pulse is applied across the two-electrode cell, of sufficient magnitude just to charge the double layer to the overpotential of the working electrode at the current density of the adjacent second pulse, which is now totally faradaic. The correct pulse-height and pulse-width ratios are found by a trial-and-error procedure. Thus, a series of potential-time transients are monitored for varying pulse-height ratios, i_1/i_2 , with pulse widths, t_1 and t_2 (t_1 is of the order of magnitude, $1 \mu\text{sec}$). Matsuda, Oka, and Delahay⁸¹ gave a detailed theoretical analysis of the method, taking into account diffusive mass transfer, which had been assumed by Gerischer and Krause⁷⁹ to be completely negligible at time t_1 . For this particular boundary-value problem, two further conditions are required besides (41)-(44), viz,

$$i_t = i_1, \quad 0 < t < t_1; \quad (82a)$$

and

$$i_t = i_2, \quad t > t_1. \quad (82b)$$

Again, the linearized Eq. (39b) is used. Although relationships of $|\eta_t| = f(t)$ have been developed for both regions, $0 < t < t_1$ and $t > t_1$, as far as the evaluation of the charge-transfer kinetic parameters is concerned, the important relationship is

$$|\eta_{t_1}| = i_2 R_{ct} \left[1 + \beta_2 t_1^{1/2} + \left(1 - \frac{9\pi}{32} \right) \beta_2^2 t_1 + \dots \right], \quad (83)$$

where

$$\beta_2 = \frac{4i_A^\circ}{3\pi^{1/2}nF} \left[\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right]. \quad (84)$$

Provided that t_1 is sufficiently short ($t_1 < 10 \mu\text{sec}$), all but the first two terms in Eq. (83) may be neglected. From the intercept at $t_1^{1/2} = 0$ of the linear plot of $|\eta_{t_1}|$ versus $t_1^{1/2}$, the charge-transfer resistance and, hence, the apparent exchange-current density may be evaluated directly.

Matsuda and Delahay⁸² have shown that, even if adsorption phenomena precede the charge-transfer step, the plots of $|\eta|$ versus $t^{1/2}$ and $|\eta_{t_1}|$ versus $t_1^{1/2}$ for the single- and double-pulse galvanostatic methods, respectively, are linear. The slopes are different from the values in the absence of adsorption, and the measured exchange current densities, i_m^o , calculated from the intercepts on the overpotential axis, are not the same as the apparent values, i_A^o .

d. Charge-step Method

An electrode-electrolyte interface may be represented by an equivalent electrical circuit, viz, two impedances in parallel: the double-layer impedance, which is purely capacitative, and the faradaic impedance, which is composed of both resistive and capacitative components. When current flows through this network, any observation of relaxation phenomena associated with the faradaic impedance, i.e., the electrode reaction, will be obscured because of the effect of the double-layer capacitance. The potentiostatic and galvanostatic step-function techniques discussed above all suffer from this practical disadvantage. As Reinmuth and Wilson⁸³ pointed out, this obscuring effect may be eliminated by employing an impulse instead of a step function as a perturbation, the relaxation phenomenon being monitored after the cessation of the pulse. During the relaxation period, when no net current flows through the cell, the charged double layer discharges through the faradaic impedance with which it is now in series. The most simple method by which a perturbing impulse can be applied to a working electrode is by allowing a charged capacitor to discharge through the cell. Barker⁸⁴ first suggested employing such a technique to study the kinetics of very rapid electrode processes. This method, which has been developed independently by Reinmuth,⁸⁵ Delahay,⁸⁶ Delahay and Aramata,⁸⁷ and Gerischer,⁸⁸ is an extension of the fast-charging potential-decay technique.⁴⁸⁻⁵³ The technique is analogous to the classical interrupter method^{9,10} for the elimination of the spurious ohmic potential drop in the study of charge-transfer processes (see Sect. V-B). It differs in that the electrolysis time before the interruption, during which appreciable net cell current flows, is negligible compared with the interruption period (relaxation time) when no net current flows and the potential-time variations are monitored. These transient variations will depend upon both the magnitude of the differential double-layer capacity and the faradaic current density. The faradaic current is governed by the faradaic impedance, which is dependent upon both the charge-transfer and the diffusive mass-transfer characteristics of the system. Since the concentrations of the reactants are intimately connected with diffusion phenomena, their absolute magnitudes will be related to the potential-time characteristics of the relaxation process. This relationship is the basis for a new electroanalytical tool, which has been developed and discussed by Delahay and his co-workers.⁸⁹⁻⁹⁵ This technique has also been applied to the study of adsorption kinetics at electrode-electrolyte interfaces.^{89,96,97} In this case,

however, during the relaxation period the charge density on the electrode remains constant, and the technique has been appropriately termed the coulometric method.

The remaining discussion will be confined to the application of this technique to the study of rapid electrode reactions. In this case, the more appropriate terminology is the charge-step method.⁸⁶

The most simple method, whereby a coulombic pulse may be applied to a working electrode, has been used successfully by Delahay and his co-workers.^{87,91,92} A low-leakage-rate, hysteresis-free, small-capacity capacitor ($\sim 300 \mu\mu\text{F}$) is charged by a d.c. source, whose emf ($\sim 10\text{-}20 \text{ V}$) is large compared with that of the working cell. By means of a fast-response wetted-mercury relay, the condenser discharges through the cell. Because the RC time constant of a cell will be of the order of magnitude, 0.1 nsec , the charging time is governed by the discharge characteristics of the external capacitor in the particular circuit. Reinmuth⁸⁵ uses a fast-rise-time square-wave generator to charge the capacitor. The overall combination of capacitor and cell, acting as an RC network, differentiates the leading edge of the applied voltage pulse, resulting in a coulombic pulse whose duration is limited by the rise-time of the generator ($\sim 0.2 \mu\text{sec}$). Delahay^{87,90} has discussed briefly a technique in which the cell is connected in series with a diode rectifier coupled to a fast-rise-time square-wave generator. In this way, coulombic pulses may be delivered to the cell in $0.1 \mu\text{sec}$. Even faster times may be achieved by employing solid-state circuitry. Minimizing the charging time minimizes the possibility of charge leakage through the faradaic impedance during charging. Since, during the relaxation period, no net current flows through the cell, it is essentially an open circuit, even though the potential of the working electrode departs from its equilibrium value as a result of the abrupt change in charge density. To obtain explicit analytic expressions for potential-time relationships in the charge-step method, when both diffusive mass-transfer phenomena and the kinetics of the charge-transfer reaction contribute to the overall control, certain assumptions must be made which necessitate setting certain conditions regarding externally-controllable parameters. Only the simple redox system (65) may be treated. The magnitude of the coulombic pulse should be such that the resulting maximum potential excursion is only of the order of a few millivolts. The linearized charge-transfer kinetic Eq. (39b) is then applicable, and for simplicity, the differential double-layer capacity is considered an invariant parameter. If q_e is the equilibrium potential charge density, q_{max} that at the maximum potential excursion, and q_t that at any time, t , after cessation of the charge step, then as $q_{\text{max}} = q_{t=0}$,

$$|\eta_t| = \frac{1}{c_{dl}} \left(\Delta q - \int_0^t i dt \right), \quad (85)$$

where Δq is the magnitude of the charging pulse equal to $|q_{\text{max}} - q_e|$.

Equations (39b) and (85) together with Eqs. (41)-(44) are the necessary boundary conditions for the solution of differential Eq. (40b). Delahay⁸⁶ has given the solution to this problem. The final overpotential-time relationship is as follows:

$$\eta_t = \frac{\Delta q}{cdl} \left\{ 1 - \frac{1}{R_{ct}cdl} \frac{1}{a-b} \left[\frac{1 - \exp(b^2 t) \operatorname{erfc}(bt^{1/2})}{b} - \frac{1 - \exp(a^2 t) \operatorname{erfc}(at^{1/2})}{a} \right] \right\}, \quad (86)$$

where the parameters a and b are given by

$$a, b = \frac{i_A^0}{2nF} \left(\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right) \pm \frac{1}{2} \left\{ \left[\frac{i_A^0}{nF} \left(\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right) \right]^2 - \frac{4}{R_{ct}cdl} \right\}^{1/2} \quad (87)$$

Reinmuth,⁷⁴ in considering diffusion-controlled charge-transfer processes, has given general equations relating the concentration of a species at the electrode surface and the faradaic current as a function of time by application of Duhamel's theorem.⁴² Using Laplace-transform techniques, he has developed an equation for the charge-step method analogous to Eq. (86). When the argument of the error-function integral is small ($at^{1/2}, bt^{1/2} \ll 1$), Eq. (86) simplifies to $\eta_{t \rightarrow 0} = \Delta q / cdl$. When the argument is large ($at^{1/2}, bt^{1/2} > 7$), Eq. (86) reduces to

$$|\eta_t| = \frac{\Delta q}{cdl} \frac{i_A^0 D_O}{\pi^{1/2}} \left(\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right) \frac{1}{t^{1/2}}. \quad (88)$$

However, in the intermediate region, Eq. (86) cannot be simplified. Reinmuth⁸⁵ points out that a useful approach is to expand this type of equation in a Maclaurin series of $t^{1/2}$. The rapidity of the convergence of the series is a measure of the overall control due to the charge-transfer reaction. The analysis of experimental data for the evaluation of the kinetic parameters will require the employment of curve-fitting techniques utilizing computer methods for the trial-and-error numerical calculations. The usefulness of the charge-step method in the evaluation of the differential double-layer capacity of an electrode-electrolyte system with an extremely high exchange current density is immediately obvious. Referring to Eq. (87), consider the expression within the braces. If this expression is large and negative, then this is tantamount to pure charge-transfer control. Under these conditions, one has the simple situation of a capacitor (electrochemical double layer) discharging through a pure resistance (charge-transfer resistance); i.e.,

$$|\eta_t| = \frac{\Delta q}{c_{dl}} \exp\left(-\frac{t}{\tau_{ct}}\right), \quad (89)$$

where τ_{ct} is the charge-transfer relaxation time,

$$\tau_{ct} = R_{ct}c_{dl}. \quad (90)$$

The apparent exchange-current density can be directly evaluated from the slope of a plot of $\log |\eta_t| - t$. The differential double-layer capacity is evaluated from the maximum potential excursion, $\eta_{t=0} = \Delta q/c_{dl}$.

If, on the other hand, the expression within the braces in Eq. (87) is large and positive, then one has pure diffusion control. In this case, the instantaneous concentrations of the species at the electrode surface are given by the Nernst Eq. (17). Equation (85) may now be expressed in terms of the flux of the species at the electrode surface by use of Eqs. (40a) and (42). The diffusion Eq. (40b) may then be solved in the usual manner with these boundary conditions and (41), (43), and (44). In this way, one obtains the following simple relationship:⁸⁵

$$|\eta_t| = |\eta_{t=0}| \exp\left(\frac{t}{\tau_D}\right) \operatorname{erfc}\left(\frac{t}{\tau_D}\right)^{1/2}, \quad (91)$$

where τ_D is the diffusional relaxation time,

$$\tau_D = \left[\frac{RTc_{dl}}{n^2F^2} \left(\frac{1}{c_{O_b}D_O^{1/2}} + \frac{1}{c_{R_b}D_R^{1/2}} \right) \right]^2. \quad (92)$$

For small values of the argument, t/τ_D , Eq. (91) simplifies to

$$|\eta_t| = |\eta_{t=0}| \left[1 - \frac{t^{1/2}}{2\pi^{1/2}\tau_D^{1/2}} \right]. \quad (93)$$

Thus, in the initial stages of the relaxation process, $|\eta_t|$ is a linear function of $t^{1/2}$ if diffusion control is maintained.

C. Alternating-current Methods

If an alternating voltage is impressed upon a cell, then the resulting interfacial potential of either of the working electrodes is compounded of three main components, as shown by Oldham.⁹⁸ First, there is a displacement of the d.c. potential from the formal equilibrium value. Second, the working-electrode potential contains a periodic component. Third, of the various harmonics of the fundamental, the first is predominant. Each of these effects may be investigated and provides powerful means of investigating the kinetics of rapid electrode reactions.

1. Faradaic Impedance

In the faradaic-impedance method, the fundamental periodic component of the working-electrode potential is studied. The relationship between the amplitudes of the alternating applied voltage and resulting

periodic current can be characterized by an impedance, which, since it has its origin in an electrochemical reaction, is referred to as the faradaic impedance,⁹⁹ and being non-inductive, is given generally by

$$Z = R - jX_c, \quad (94)$$

where $j = (-1)^{1/2}$. The resistive and capacitive components of this complex impedance may be considered to be in series or parallel. The electrode-electrolyte interface may be represented by the equivalent circuits (Figs. 7A and 7B): the double-layer capacity in parallel with the faradaic impedance. The series faradaic-impedance network (Fig. 7A) is more amenable to mathematic analysis. However, since some investigations in this field have employed the parallel network (Fig. 7B),

Fig. 7. Electrochemical Equivalent Circuits

for example, Falk and Lange¹⁰⁰ and Gerischer,^{101, 102} the interrelationships will be given. Denoting the series and parallel networks with the subscripts s and p , respectively, and remembering that impedances are combined in the same manner as resistances, one has, from Eq. (94),

$$Z_s = R_s - \frac{j}{\omega C_s}, \quad (95)$$

and

$$\frac{1}{Z_p} = \frac{1}{R_p} + j\omega C_p, \quad (96)$$

where ω , the angular frequency is given by $2\pi f$, and f is the frequency of the applied signal. For the two networks to be equivalent, $Z_s = Z_p$. Therefore, from Eq. (95) and (96),

$$\frac{Z_s}{Z_p} = \frac{R_s}{R_p} + \frac{C_p}{C_s} - j\left(\frac{1}{\omega C_s R_p} - \omega C_p R_s\right) = 1. \quad (97)$$

Separately equating the real and imaginary parts, one has

$$\frac{c_p}{c_s} = 1 - \frac{R_s}{R_p}, \quad (98)$$

$$c_p c_s = \frac{1}{\omega^2 R_p R_s}, \quad (99)$$

and finally,

$$R_p = R_s [1 - (\omega R_s c_s)^{-2}], \quad (100)$$

and

$$c_p = c_s [1 + (\omega R_s c_s)^2]^{-1}. \quad (101)$$

R_s and c_s have been called the polarization resistance and the pseudo-capacitance, respectively.^{19,95} If the applied a.c. signal is such that the resulting fundamental periodic electrode potential has an amplitude not exceeding a few millivolts, then one may neglect the harmonics. Furthermore, if one of the working electrodes is essentially unpolarizable, then, when the cell is placed in one arm of a Wien impedance bridge, the charge-transfer resistance²⁷ and, hence, the apparent exchange-current density may be evaluated from the magnitude of the resistive and capacitive components of the balancing-arm impedance.

The theory of faradaic impedance has been discussed by various authors.^{77,98-108} Essentially, one solves Eq. (40b) with boundary conditions (41)-(44) and the linearized charge-transfer kinetic Eq. (39b). The current-voltage characteristic of a series R_s - c_s circuit, when the sinusoidal applied voltage takes the form $V = V_0 \sin \omega t$, is given by

$$V = I[R_s \sin \omega t + (\omega c_s)^{-1} \cos \omega t]. \quad (102)$$

In the steady state [i.e., when $(\omega t)^{1/2} \gg 1$], and neglecting the effects of the electrolyte resistance, R_{soln} , and the double layer, one obtains, as the solution of Eq. (40b),

$$|\eta| = i[(R_{ct} + Q/\omega^{1/2}) \sin \omega t + Q/\omega^{1/2} \cos \omega t], \quad (103)$$

where

$$Q = \frac{RT}{2^{1/2} n^2 F^2} \left[\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right]. \quad (104)$$

The analogy between Eqs. (102) and (103) is obvious. Therefore, per unit area of electrode surface,

$$R_s = R_{ct} + R_{mt} = \frac{RT}{nFi_A^0} + \frac{RT}{n^2F^2(2\omega)^{1/2}} \left[\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right]; \quad (105)$$

and

$$c_s = c_{mt} = \frac{2^{1/2} n^2 F^2}{RT \omega^{1/2}} \left[\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right]^{-1} \quad (106)$$

The total contribution to the faradaic impedance due to diffusive mass-transfer phenomena may be embodied in the Warburg impedance;¹⁰⁹⁻¹¹¹ viz,

$$|W| = [R_{mt}^2 + (\omega c_{mt})^{-2}]^{1/2}. \quad (107)$$

Thus, the faradaic impedance may also be represented by the series combination of the charge-transfer resistance and the Warburg impedance (Fig. 7C). If the bulk concentration of species O is dependent upon a homogeneous chemical equilibrium of type (72), then, as shown by Gerischer,¹⁰¹ reaction polarization must be considered. If the production of O is a first- or pseudo-first-order process, and furthermore, for simplicity, if it is assumed that $D_N = D_O$, then the resistive and capacitive terms expressed by Eqs. (108) and (109) must be added to the right-hand side of Eqs. (105) and (106), respectively:

$$R_{rp} = \frac{RT c_{N_b}}{(2D_O^{1/2})(nF)^2 c_{O_b} (c_{O_b} + c_{N_b})} \left\{ \frac{[\omega^2 + (k_f + k_r)^2]^{1/2} + (k_f + k_r)}{\omega^2 + (k_f + k_r)^2} \right\}^{1/2}; \quad (108)$$

$$c_{rp} = \frac{(2D_O)^{1/2} (nF)^2 c_{O_b} (c_{O_b} + c_{N_b})}{RT c_{N_b}} \left\{ \frac{[\omega^2 + (k_f + k_r)^2]^{1/2} - (k_f + k_r)}{\omega^2 + (k_f + k_r)^2} \right\}^{-1/2}. \quad (109)$$

Gerischer¹⁰² has also shown that analogous behavior prevails when the charge-transfer step is preceded by a heterogeneous chemical step.

The alternating current through R_s , which is in phase with the sinusoidal input voltage, lags behind that through c_s . The vectorial addition of the components of the faradaic impedance,³³ viz, R_s and $(\omega c_s)^{-1}$, results in the following simple relationship for the phase angle:

$$\theta_1 = \arccot(\omega R_s c_s). \quad (110)$$

When reaction-polarization effects are in evidence, as can be seen from Eqs. (105)-(110), the dependence of R_s , c_s , and θ upon frequency is quite complicated. In the limit, as $\omega \rightarrow 0$, $c_{rp} \rightarrow 0$ and R_{rp} becomes frequency-independent, approaching the constant value

$$R_{rp}(\omega \rightarrow 0) = \frac{RTc_{N_b}}{D_O^{1/2}(nF)^2 c_{O_b}(c_{O_b} + c_{N_b})(k_f + k_r)^{1/2}} \quad (111)$$

In the limit, as $\omega \rightarrow \infty$, $c_{rp} \rightarrow 0$ and $R_{rp} \rightarrow 0$. Therefore, if R_s is plotted as a function of $\omega^{-1/2}$ over a wide frequency range, both the apparent exchange current density and the factor $(k_f + k_r)$ may be evaluated. In the absence of reaction polarization, a plot of $(\omega c_s)^{-1}$ as a function of $\omega^{-1/2}$ should be linear, whereas a maximum is observed when reaction polarization is in evidence.¹⁰¹

The effects of the double layer and specific adsorption of reactants on the faradaic impedance have been considered by various workers¹¹² (see Senda and Delahay¹¹³ for details). The findings may best be described by modifying the equivalent circuit (Figs. 7D and 7E). Specific adsorption of species "q" is accounted for by adding a resistance R_A^q in series with W and a capacitance c_A^q in parallel with this series combination. According to whether there is repulsion or attraction of the discharging species by the double layer, a resistance R_{dl}^i in series with, or a capacitance c_{dl}^i in parallel with, the Warburg impedance must be added. Both R_{dl}^i and c_{dl}^i are directly proportional to an exponential function of the inner potential difference²⁰ across the diffuse part of the double layer and inversely proportional to its thickness, and are frequency-independent. Their influences, however, become increasingly less important with decrease in frequency. The influence of R_A^q and c_A^q depends upon adsorption characteristics, the latter being governed by the actual equilibrium, whereas the former is governed by the kinetics of the adsorption process.

The electrostatic approach to the general problem of the effect of activation polarization on the a.c. characteristics of the electrode-electrolyte interface has received relatively little attention compared with the approach outlined above.

In 1952, Chang and Jaffé¹¹⁴ generalized Jaffé's original theory of conduction in polarizable media,¹¹⁵ taking into account ionic discharge as a rate process. The theory was developed in terms of the polarization layer concept. Differential equations, with the necessary boundary conditions, relating species concentration, permittivity, and field strength within the layer, were set up and solved. The parallel network (Fig. 7B) was employed to simulate the electrode-electrolyte interface. The final equations, however, were transposed to the equivalent series network (Fig. 7A). The resistance and capacitive reactance, i.e., the real and imaginary components of the complex impedance, were given in terms of the values at infinitely high frequency, the diffusion coefficient, the angular frequency, and the thickness of

the polarization layer. Expressions were also given relating this latter parameter as a function of frequency. The validity of the theory was experimentally verified by Jaffe' and Rider.¹¹⁶

Considerable success has been achieved in applying general relaxation theory to the evaluation of rate constants of rapid ionic reactions in various electrolyte systems.¹¹⁷ De Maeyer and Kustin¹¹⁸ have reviewed the entire field of rapid reactions. Eigen and de Maeyer¹¹⁹ have discussed the various relaxation experimental techniques. The behavior of the complex impedance of a cell in an a.c. field will be governed by the a.c. characteristics of the electrode-electrolyte interfaces, which, in turn, are governed by the nature and rate of the charge transfer and possible associated chemical reactions, giving rise to the total activation polarization. The relationships governing the impedance as a function of frequency may be obtained by utilizing the well-known electrostatic relaxation-dispersion theory relationships governing the complex permittivity as a function of frequency. This treatment of the faradaic impedance was first given by Brodd,¹²⁰ who pointed out that, with regard to electrochemical systems, the Argand diagram method of representing experimental data¹²¹ is very informative. Brodd and DeWane¹²² employed the theory to interpret impedance data for various battery systems. As Brodd only gives the final relationships for the polarization resistance and pseudocapacitance as functions of frequency, the theory is outlined below.

The polarization vector, $\vec{P}$, which is a measure of the number of apparent dipoles in the electrode-electrolyte interface resulting from electric field distortions when the flow of charged species is impeded by a relatively slow charge-transfer phenomenon, is defined by¹²³

$$\text{div } \vec{P} = -\rho', \quad (112)$$

where ρ' is the volume density of induced bound charges. If σ and ρ represent the surface and volume free-charge densities, respectively, then the displacement and field strength vectors, $\vec{D}$ and $\vec{E}$, are defined by Maxwell's equation. Using the rational mks system of units results in

$$\epsilon^\circ \cdot \text{div } \vec{E} = \rho + \rho', \quad (113)$$

and

$$\text{div } \vec{D} = \rho, \quad (114)$$

where ϵ° is the permittivity of a vacuum, whose value is governed by the choice of units. In this case, $\epsilon^\circ = 0.08854 \mu\text{F}/\text{cm}$. The displacement, which is also the surface free-charge density, is related to the field strength, by means of the permittivity (dielectric constant):

$$\sigma = \vec{D} = \epsilon \vec{E}. \quad (115)$$

From Eqs. (112)-(114), one obtains the well-known relationship,

$$\vec{P} = \vec{D} - \epsilon \vec{E}. \quad (116)$$

When the electrode-electrolyte interface is subjected to an alternating electric field, two possibilities exist, which depend upon the frequency of the applied field, the temperature, and the properties of and behavior at the interface. The vectors, $\vec{D}$, and hence, $\vec{P}$, may be in or out of phase with $\vec{E}$. Energy will be absorbed at the interface as a result of the charge-transfer process proceeding in one direction at a finite rate. This leads to the out-of-phase condition. In such cases, complex-number notation is used to describe the displacement and electric-field vectors in terms of scalar amplitudes. It is also necessary to define a complex permittivity. Thus, one has

$$\hat{D} = \hat{\epsilon} \hat{E}, \quad (117a)$$

and

$$D_0 e^{j(\omega t - \theta)} = \hat{\epsilon} E_0 e^{j\omega t}, \quad (117b)$$

where θ is the phase angle.

If a static electric field is established across an electrode-electrolyte interface, the perturbation causes a change in the equilibrium distribution of the electroactive species in the region contiguous with the interface; i.e., the electrode is polarized. The growth of polarization on application of the field and the decay on cessation are rate processes, which may be described by the differential equations,

$$d\vec{P}_t/dt = (\vec{P}_{\text{final}} - \vec{P}_t)/\tau, \quad (118a)$$

and

$$-d\vec{P}_t/dt = \vec{P}_t/\tau, \quad (118b)$$

where τ is a constant having the dimensions of time and is called the relaxation time. The polarization rate process and its development were first described by Pellat.^{124, 125} Although strictly applicable to static fields, it may be applied to alternating fields with not too high a frequency ($f < 1$ Mc/sec). In the steady state, i.e., after a few cycles, Eq. (117a) may be expressed in the following form (see Böttcher,¹²³ p. 348; see also Smyth,¹²⁶ Fröhlich,¹²⁷ and Debye¹²⁸):

$$\hat{D} = \left(\epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau} \right) \hat{E}. \quad (119)$$

From Eq. (117b), one has

$$\hat{\epsilon} = [D_0/E_0] \cos \theta - j[D_0/E_0] \sin \theta = \epsilon' - j\epsilon'', \quad (120)$$

where ϵ' is the real permittivity, and the imaginary component, ϵ'' , is referred to as the loss factor. From Eqs. (117a), (119), and (120), one obtains the well-known Debye relationships:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2 \tau^2}, \quad (121a)$$

and

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty) \frac{\omega \tau}{1 + \omega^2 \tau^2}, \quad (121b)$$

where ϵ_0 and ϵ_∞ are the real permittivities at frequencies much less than, and much greater than, $1/2\pi\tau$, respectively.

Consider the application of an alternating voltage, $V = V_0 \sin \omega t$, to an electrode-electrolyte interface. Although $E = \text{grad } V$, for simplicity consider only the direction normal to the interface. If d is the width of this region (the polarization-layer thickness) then $V = E/d$. The field strength at the interface, $E_0 \sin \omega t$, corresponds to the imaginary component of the complex field strength. From Eq. (115), the resulting current density is given by

$$i = \frac{d}{dt} [D_0 \sin (\omega t - \theta)] = D_0 \cos \theta \cdot \omega \cos \omega t + D_0 \sin \theta \cdot \omega \sin \omega t. \quad (122)$$

From Eq. (117b), $D_0 \cos \theta = \epsilon' E_0$, and $D_0 \sin \theta = \epsilon'' E_0$; hence,

$$i = [\omega \epsilon'' \sin \omega t + \omega \epsilon' \cos \omega t] V_0/d. \quad (123)$$

It is easily shown that the rate of energy absorption per unit volume of interface region is $\omega \epsilon'' E_0^2/2$; i.e., it is related only to the in-phase component of i . It may also be shown that the current-voltage characteristics of the equivalent series and parallel networks (Figs. 7A and 7B) are

$$I = [(R_s/|Z_s|^2) \sin \omega t + (X_s/|Z_s|^2) \cos \omega t] V_0, \quad (124)$$

and

$$I = [(1/R_p) \sin \omega t + (1/X_p) \cos \omega t] V_0. \quad (125)$$

where X_s and X_p are the series and parallel capacitive reactances, $1/(\omega c_s)$ and $1/(\omega c_p)$, respectively, and $|Z_s|$ is the absolute magnitude of the complex series impedance, $(R_s^2 + X_s^2)^{1/2}$. The complex impedance per unit area of electrode-electrolyte interface may be related to the complex permittivity by comparing Eq. (123) with Eqs. (124) and (125). One finds,

$$Z_s = \frac{|Z_s|^2}{d} \cdot j\omega\epsilon, \quad (126a)$$

$$R_s = \frac{|Z_s|^2}{d} \omega\epsilon'', \quad (126b)$$

$$X_s = \frac{|Z_s|^2}{d} \omega\epsilon', \quad (126c)$$

$$Z_p = d/(j\omega\epsilon), \quad (127a)$$

$$R_p = d/(\omega\epsilon''), \quad (127b)$$

and

$$X_p = d/(\omega\epsilon'). \quad (127c)$$

Brodd¹²⁰ uses the equivalent parallel circuit. As can be seen from Eqs. (120), (126), (127), and (110),

$$\tan \theta_2 = \frac{\epsilon''}{\epsilon'} = \frac{X_p}{R_p} = \frac{R_s}{X_s} = \cot \theta_1. \quad (128)$$

As Cole and Cole¹²¹ showed, if one constructs the Argand diagram or complex plane locus, by plotting the loss factor versus the real permittivity, then, if there is only one relaxation process occurring in the range of frequencies covered, a semicircle results whose center lies on the real permittivity axis at a distance of $1/2(\epsilon_0 + \epsilon_\infty)$ from the origin, of radius $1/2(\epsilon_0 - \epsilon_\infty)$. By analogy, for one relaxation-electrode process, a plot of the capacitive reactance versus the resistance, as measured on a Wien impedance bridge,¹²⁹ yields a similar semicircle. Hence, these parameters may be given as functions of frequency by equations analogous to Eqs. (119)-(121); viz,

$$Z = R_\infty + \frac{R_0 - R_\infty}{1 + j\omega\tau} \quad (129)$$

$$R = R_\infty + \frac{R_0 - R_\infty}{1 + \omega^2\tau^2} \quad (130)$$

and

$$X = (R_0 - R_\infty) \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (131)$$

On the mks system, the units of Z , R , and X are ohms-meter². At frequencies very much lower or higher than the absorption region, the impedance is essentially constant and is purely resistive in nature. Thus, the difference parameter, $R_0 - R_\infty$, is a direct measure of the charge-transfer resistance²⁷ of the rate-determining electrode process. Therefore, the exchange current density, characteristic of this step, is given by

$$i_A = RT/[\lambda F(R_0 - R_\infty)]. \quad (132)$$

Experimentally, one may find that the Argand plot is a distorted semicircle. This is because more than one relaxation process is contributing to the dispersion phenomena. In this case, the complex impedance must be given by the general relationship,

$$Z = R_\infty + (R_0 - R_\infty) \int_0^\infty \frac{G(\tau) d\tau}{1 + j\omega\tau} \quad (133)$$

Various theoretical and empirical expressions have been proposed for the relaxation time-distribution function, $G(\tau)$.^{123, 126} One of the most successful and widely used is the Cole-Cole function,¹²¹

$$G(\tau) = \frac{1}{2\pi} \left[\frac{\sin m\pi}{\cosh[(1-m)\tau] - \cos m\pi} \right], \quad 0 < m < 1. \quad (134)$$

This leads to the following simple modifications of Eqs. (129)-(131):

$$Z = R_\infty + \frac{R_0 - R_\infty}{1 + (j\omega\tau)^{1-m}}, \quad (135)$$

$$R = R_\infty + \frac{R_0 - R_\infty}{1 + (\omega^2\tau^2)^{1-m}}, \quad (136)$$

and

$$X = (R_0 - R_\infty) \frac{j^{-m}(\omega\tau)^{1-m}}{1 + (\omega^2\tau^2)^{1-m}}. \quad (137)$$

In this case, a plot of X as ordinate against R as abscissa yields a minor arc of a circle, of radius

$$\left(\frac{R_0 - R_\infty}{2}\right) \operatorname{cosec} (1 - m) \pi/2,$$

whose center lies at a distance

$$\left(\frac{R_0 - R_\infty}{2}\right) \cotan (1 - m) \pi/2$$

below the R axis. The arc crosses the R axis at distances R_∞ and R_0 from the origin. It may be shown^{123, 126} that, if U_n and V_n are the lengths of the lines from the arc crossing points, R_∞ and R_0 , respectively, to any point on the arc, corresponding to angular frequency, ω_n , then

$$\log_{10}[V_n/U_n] \propto (1 - m) \log_{10}\omega_n. \quad (138)$$

Thus, m may be determined directly from this log-log plot. The closer m is to unity, the greater the number of separate relaxation processes. Brodd¹²⁰ and Brodd and DeWane¹²² employ a different approach. They assume that the total polarization is the sum of the separate polarizations characteristic of each separate relaxation process; i.e., they define the complex impedance by the summation expression,

$$Z = R_\infty + \sum_r \frac{(R_0 - R_\infty)_r}{1 + j\omega\tau_r}, \quad (139)$$

where the subscript refers to the r^{th} relaxation process. Semicircles of varying radii and varying position on the resistance axis are combined to fit the experimental Argand diagram. From each semicircle, $(R_0)_r$ and $(R_\infty)_r$ are evaluated. The relaxation may then be evaluated from Eqs. (130) and (131).

A second way of presenting and analyzing experimental data is to plot the normal dispersion and absorption curves; i.e., plot R and X , respectively, as functions of $\log \omega$. For a single relaxation process, the plot of R versus $\log \omega$ is a fairly sharp sigmoid curve, whose maximum slope occurs when $\omega = 1/\tau$ at $R = (R_0 + R_\infty)/2$. The plot of X as a function of ω reaches a maximum value of $(R_0 - R_\infty)/2$ at $\omega_{\text{max}} = 1/\tau$. The presence of more than one relaxation process shows its effect in a flattening and broadening of the dispersion and absorption curves.

2. Faradaic Rectification

The assumption that the curve of current density versus electrode potential is linearly symmetrical about the formal equilibrium potential at low current densities is not strictly true. Because of this asymmetry, two further effects are observed when an alternating signal is applied to an electrode-electrolyte system. If the periodic input is purely sinusoidal, i.e., is free from harmonics, then the electrode potential is displaced from its

equilibrium value. This effect was first observed by Doss and Agarwal,¹³⁰ who coined the name Redoxokinetic effect. The alternating component of the resulting electrode potential consists of a component of the same frequency as the input signal, a first-harmonic component (twice the frequency of the input signal), and a rectified first-harmonic component. The displacement of the d.c. potential from the equilibrium value is now known to be due to the coupling of this rectified component with the fundamental alternating component. Oldham¹³¹ gave the most appropriate name describing this effect, viz, faradaic rectification.

If the cell is connected to the a.c. generator by means of a leak-free capacitance, then the d.c. resistance of the entire circuit is infinite.

Fig. 8. Explanatory Diagram for Faradaic Rectification

Thus, the mean value of the total cell current is zero. Neglecting for the moment the charging of the double layer, this implies that the mean faradaic current is zero. Consequently, as there is no net electrode reaction, there is no mass-transfer polarization. From Fig. 8, the result of the coupling of the fundamental a.c. component and the rectified first-harmonic component of the electrode potential is that the average value of the electrode potential, $\bar{E}_t$, is displaced from E_c . This displacement, ΔE_∞ , is referred to as the faradaic rectification voltage. Since the differential capacity of the double layer is not negligible, the total current is given by the sum of

the faradaic and double-layer charging currents, neither of which is necessarily zero. It may be shown⁸⁴ that the result of a finite mean charging current is to cause variations in electrode-surface concentration. Thus, there is mass-transfer polarization. As the differential double-layer capacity is potential-dependent, the faradaic rectification effects a variation in c_{dl} , which in turn effects a further potential displacement, ΔE_{dl} , referred to as the nonfaradaic rectification voltage.^{84,139} If it is desired to work under such conditions that the total rectification voltage is zero, then by an external means this voltage must be compensated by an opposing voltage shift. As can be seen from Fig. 8, this results in a direct current, i_R , flowing. This is referred to as the faradaic rectification current. Thus, a net electrode reaction proceeds, the resulting variations in electrode-surface concentration effecting a shift of the equilibrium potential, E_e , to a limiting value, $E_{e,lim}$.

Theoretical investigations of faradaic rectification all start by considering the asymmetry of the polarization curves near E_e . Initially, the rectification was treated as a second-order perturbation; i.e., the η_{ct}^2 terms in the expansion of the exponentials in Eq. (39a) were included^{84, 130, 137}. For any electrochemical process, for small perturbations such that the linearized Eq. (39b) may be employed, the variation in the current density due to variations in the electrode potential and in the concentrations of reactive species, may be written in the general form:

$$\delta p_i = (\partial i / \partial E) \delta_p E + (\partial i / \partial c_O) \delta_{pcO} + (\partial i / \partial c_R) \delta_{pcR}. \quad (140)$$

Grahame employed this approach in his treatment of faradaic impedance.⁹⁹ Delahay, Senda, and Weiss¹³⁸ extend this approach to take into account the nonlinearity of polarization curves by adding a second-order correction term, $\delta_p^2 i$, to the right-hand side of Eq. (140). The total current-density variation, δi , is given by

$$\delta i = \delta_0 i + \delta_1 i + \delta_2 i. \quad (141)$$

These three terms, $p = 0, 1$, and 2 correspond to the mean d.c., fundamental a.c., and first-harmonic a.c., component, respectively. One either works under mean current control, $\delta_0 i = 0$, and measures the faradaic-rectification voltage, $\delta_0 E \equiv \Delta E_\infty$, or under mean potential control, $\delta_0 E = 0$, and measures the faradaic-rectification current density, $\delta_0 i \equiv i_R$.

When the rectification effect is observed under mean current control, $\delta_0 i = 0$, at any instantaneous time, the situation is analogous to the effect produced by application of a charge pulse (see Par. IX-B-3-d on the charge-step method). The double layer is charged to full capacity and discharges through the faradaic impedance. The complete expression for the total rectification voltage as a function of time for any one frequency of a.c. input is similar to that given for the overpotential-time relationship in the charge-step method, Eq. (86), viz,

$$\Delta E_t = \Delta E_\infty + \left[\frac{\Delta E_\infty - \Delta E_{dl}}{\tau_{ct}} \right] \frac{1}{a - b} \left[\frac{\exp(a^2 t) \operatorname{erfc}(at^{1/2})}{a} - \frac{\exp(b^2 t) \operatorname{erfc}(bt^{1/2})}{b} \right], \quad (142)$$

where the parameters a and b are given by Eq. (87), τ_{ct} is given by Eq. (90), ΔE_{dl} and ΔE_∞ , the nonfaradaic^{84, 139} and final-faradaic¹³⁰ rectification voltages, are given by

$$\Delta E_{dl} = -\frac{V_0^2}{4c_{dl}} \cdot \frac{dc_{dl}}{dE}, \quad (143)$$

and

$$\Delta E_{\infty} = \frac{nFV_0^2}{RT} \left[\frac{2\alpha - 1}{4} - \frac{1}{2} \left(\alpha - \frac{c_{O_b} D_O^{1/2}}{c_{O_b} D_O^{1/2} + c_{R_b} D_R^{1/2}} \right) \left(\frac{1 + \cot \theta_1}{1 + \cot^2 \theta_1} \right) \right], \quad (144)$$

where V_0 is the amplitude of the a.c. input signal, α is the transfer coefficient (Sect. VII), ω is the angular frequency, and θ_1 is the apparent phase angle, in the absence of adsorption phenomena and neglecting double-layer effects, given by Eq. (110).

When the faradaic-rectification current is to be related as a function of time under mean potential control, it is necessary to allow for the ohmic potential drop through the cell and circuit in the compensating voltage. The analysis of the boundary-value problem is exactly analogous to that for the voltage-step method⁴⁵ (see Par. IX-B-2-b), and the relationship of current density to time is given by Eqs. (58) and (59) with $\Delta V = -\Delta E_{\infty}$. Thus, as in the voltage-step method, the current is primarily determined by R_t , when $R_t \gg R_{ct}$.

For large values of t , the expressions for ΔE_t and i_R simplify to

$$\Delta E_t = \Delta E_{\infty} - (\Delta E_{\infty} - \Delta E_{dl}) \frac{i_A^{\circ} D_O}{\pi^{1/2}} \left(\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right) \frac{1}{t^{1/2}}, \quad (145)$$

and

$$i_R = \Delta E_{\infty} \frac{n^2 F^2}{RT} \left(\frac{1}{c_{O_b} D_O^{1/2}} + \frac{1}{c_{R_b} D_R^{1/2}} \right)^{-1} \left(\frac{1}{\pi t} \right)^{1/2}. \quad (146)$$

The faradaic rectification voltage, ΔE_{∞} , may be evaluated by direct and indirect methods. The direct method utilizes Eq. (146) which, for large values of t when there is pure diffusion control, is valid irrespective of the relative values of R_t and R_{ct} . The indirect method, which was first proposed by Barker,⁸⁴ has been discussed in detail and experimentally verified by Senda, Imai, and Delahay.¹⁴⁰ Current density-time variations are monitored by means of the faradaic-rectification technique and the voltage-step method, the step voltage being adjusted so that the two curves are superimposable. Hence, $\Delta E_{\infty} = -\Delta V$.

The kinetic parameters, α and i_A° , may be evaluated by investigating the frequency dependence of ΔE_{∞} . In the absence of specific adsorption of reactants, and neglecting the effect of the double layer, the apparent phase angle, given by Eq. (110), may be written in the form

$$\arccot [1 + \omega^{1/2} / (Q i_A^{\circ})],$$

where Q is given by Eq. (104). As $\omega \rightarrow 0$, $\cot \theta_1 \rightarrow 1$, and diffusive mass-transfer control becomes increasingly predominant. From Eq. (144), one obtains

$$\frac{\Delta E_\infty}{V_0^2} = \frac{nF}{4RT} \left(\frac{c_{O_b} D_O^{1/2} - c_{R_b} D_R^{1/2}}{c_{O_b} D_O^{1/2} + c_{R_b} D_R^{1/2}} \right) \quad (147)$$

When one controls either the mean direct current, $\delta_0 i = 0$, or the mean rectification voltage, $\delta_0 E = 0$, one controls simultaneously either the alternating component of the current density (a.c. control) or the alternating component of the voltage (a.v. control). The relationships derived for ΔE_∞ and i_R are independent of the type of alternating control.¹³⁸ However, the amplitude of the alternating cell voltage, V_0 , for a given alternating-current input, amplitude I_0 , does depend upon whether one works under a.c. or a.v. control. If the faradaic impedance, Z_f , is much greater than the capacitive reactance of the double layer, $X_{dl} = 1/(\omega c_{dl})$, then one has a.v. control, and since $V_0 \approx I_0/(\omega c_{dl})$, then $\Delta E_\infty/I_0^2 \propto 1/\omega^2$. If, on the other hand, $Z_f \ll X_{dl}$, then one has a.c. control, and since $V_0 \approx I_0 Z_f$ and $Z_f \propto 1/\omega^{1/2}$, then $\Delta E_\infty/I_0^2 \propto 1/\omega$. A plot of $\log[\Delta E_\infty/I_0^2]$ as a function of $\log \omega$, for low values of ω , will indicate the relation magnitudes of Z_f and X_{dl} . As $\omega \rightarrow \infty$, $\cot \theta_1 \rightarrow \infty$, and charge-transfer control becomes increasingly predominant, and

$$\frac{\Delta E}{V_0^2} = \frac{nF(2\alpha - 1)}{4RT} - \frac{i_A^0}{2^{3/2}RT} \left[\frac{(\alpha - 1) c_{O_b} D_O^{1/2} + \alpha c_{R_b} D_R^{1/2}}{c_{O_b} D_O^{1/2} + c_{R_b} D_R^{1/2}} \right] \frac{1}{\omega^{1/2}} \quad (148)$$

Thus, at high frequencies, a plot of $\Delta E_\infty/V_0^2$ as a function of $1/\omega^{1/2}$ is a linear curve, whose slope yields i_A^0 and intercept yields α , provided D_O and D_R are known.

When a chemical reaction precedes the charge-transfer process, then the equations for ΔE_∞ and i_R have to be modified. The resistive and capacitive terms, Eqs. (108) and (109), have to be added to the polarization resistance, R_s , and the pseudocapacitance, c_s , as in the theory of faradaic impedance.¹³⁸ The effects of the double-layer, specific, and nonspecific adsorption of reactants are treated in a manner analogous to the treatment of faradaic impedance.¹¹³

3. Faradaic Distortion

The component of the complex electrode-electrolyte potential, resulting from the application of a pure sinusoidal input signal, due to the predominating first harmonic, is referred to as the faradaic-distortion voltage. Oldham,⁹⁸ who coined the term, has discussed this phenomenon in detail and derived expression for the amplitude, V_{ofd} , and phase angle, θ_{fd} ,

taking into account the effect of the double layer. The mathematical analysis, involving Laplace-transform methods, is similar to that used in the above-discussed perturbation techniques. Only the final expressions are given:

$$V_{ofd} = \frac{nFV_0^2}{4RT} \left(\frac{\Gamma^2 + 2\Gamma + 2}{\Lambda^2 + 2\Lambda + 2} \right)^{1/2} \frac{\Omega}{[(\Lambda + 2^{-1/2})^2 + (\Omega + 2^{-1/2})^2]^{1/2}}; \quad (149)$$

and

$$\cot \theta_{fd} = \frac{(\Lambda + 2^{-1/2})(\Lambda + \Gamma + 2) - (\Omega + 2^{-1/2})(\Lambda + \Omega + \Lambda\Omega)}{(\Omega + 2^{-1/2})(\Lambda + \Gamma + 2) + (\Lambda + 2^{-1/2})(\Lambda + \Omega + \Lambda\Omega)}; \quad (150)$$

where

$$\Lambda = \frac{(2\omega)^{1/2} nF}{i_A^0} \left(c_{O_b} D_O^{1/2} + c_{R_b} D_R^{1/2} \right), \quad (151)$$

$$\Omega = \Lambda / (2\omega R_{ct}), \quad (152)$$

and

$$\Gamma = (1 - 2\alpha) \Lambda \left(\frac{c_{O_b} D_O^{1/2} + c_{R_b} D_R^{1/2}}{c_{O_b} D_O^{1/2} - c_{R_b} D_R^{1/2}} \right). \quad (153)$$

The faradaic distortion voltage is then given by

$$V_{fd} = V_{ofd} \sin(2\omega t + \theta_{fd}). \quad (154)$$

The parameter Ω is a measure of the ratio of the double-layer impedance to the faradaic impedance; Ω decreases with increasing frequency; i.e., the faradaic distortion is shorted out by the double-layer impedance. With decreasing frequency, Ω and, hence, Λ increase. In the limit, when Ω , Λ , and $\Gamma \ll 1$,

$$V_{ofd} = \frac{nFV_0^2}{4RT} (2\alpha - 1) \left(\frac{c_{O_b} D_O^{1/2} + c_{R_b} D_R^{1/2}}{c_{O_b} D_O^{1/2} - c_{R_b} D_R^{1/2}} \right). \quad (155)$$

Thus, one sees from Eqs. (147) and (155) that, in the limit as $\omega \rightarrow 0$, there is an inverse relationship between the faradaic-rectification voltage and the amplitude of the faradaic-distortion voltage, as follows:

$$\left(\frac{\Delta E_\infty}{V_0^2} \right)_{\omega \rightarrow 0} = \left(\frac{nF}{4RT} \right)^2 (1 - 2\alpha) \left(\frac{V_{ofd}}{V_0^2} \right)_{\omega \rightarrow 0}^{-1}. \quad (156)$$

However, on the contrary, as $\omega \rightarrow \infty$, there is a direct relationship between ΔE_∞ and V_{ofd} . From Eqs. (148) and (149),

$$\left(\frac{\Delta E_\infty}{V_0^2} \right)_{\omega \rightarrow \infty} = (2\alpha + 1) \left(\frac{V_{\text{ofd}}}{V_0^2} \right)_{\omega \rightarrow \infty} \quad (157)$$

The faradaic-distortion method offers advantages over the faradaic-impedance method for the determination of the kinetic parameters, α and i_A^0 , in that a knowledge of the differential double-layer capacity is not required, in contrast to the faradaic-rectification method. However, use of the faradaic-distortion method is severely limited, in that only a limited concentration range of reactants is available. The upper limit is set by the fact that the supporting electrolyte must be present in large excess. The lower limit is set by the fact that the double-layer shorting effect, especially at low frequencies, becomes very pronounced at low concentrations. Oldham⁹⁸ tabulates the concentration and frequency limits applicable in aqueous solution at room temperature.

X. EXPERIMENTAL METHODS

Paralleling the advances made in applying operational mathematics to the theoretical principles underlying the diverse sophisticated techniques discussed, are the achievements in the field of electrochemical instrumentation. A detailed discussion of the precise experimental methods associated with each of the various techniques discussed above is beyond the scope of this review.

Overall simplicity and symmetrical location of working electrodes is of prime importance in designing the working cell. All cell components should be absolutely clean, and purity of the solvent and electrolyte system is essential. If possible, an electrolyte with a high conductivity should be chosen, and the total of the cell internal and circuit resistances should be minimized. This is of prime importance if the voltage step is to be employed, or if the faradaic-rectification voltage is to be evaluated by the indirect voltage-step comparison procedure (see Par. IX-B-2-b). In the single- and double-pulse galvanostatic methods, the ohmic drop in the cell, which is greater than the electrode potential changes in the early stages of electrolysis, is corrected for by including a compensating bridge between the galvanostat and the cell.^{46, 78, 81} When solid electrodes are employed, as is more often the case when electrochemical investigations are performed in molten-salt media, they should be hydraulically smooth, since convective flow and the double-layer capacity are greatly affected by the surface state of the electrode. The main disadvantage of the voltage-step method, besides the limitations imposed by the ohmic drop through the cell and the external circuit, is the relatively long time required for charging and discharging the double layer. This time is appreciably shorter in the potential-step method and, therefore, the condition that $\phi_1 t^{1/2} \ll 1$, which is necessary for the simplification of Eq. (56) is more easily satisfied for larger values of i_A^0 than is the condition that $\phi_2 t^{1/2} \ll 1$ which is necessary for the simplification of Eq. (58). Thus, values of i_A^0 of the order of magnitude 10^{-2} Amp/cm² can be measured by the voltage-step method, whereas apparent exchange-current-density values of the order of magnitude 10^{-1} Amp/cm² may be evaluated by the potential-step method. Values of i_A^0 of the order of magnitude 10^{-1} may also be measured by the single-pulse galvanostatic method, which has the added advantage of being an inherently more simple experimental technique. The charge-step method, which offers the same potentialities as the single-pulse galvanostatic procedure, has the added advantage of even greater simplicity of both technique and interpretation of data. Furthermore, of fundamental importance is the fact that, by this technique, the double-layer capacity can be measured directly, even when the charge-transfer process is extremely rapid, whereas in the voltage-step, potential-step, faradaic-impedance, distortion, and rectification methods, this parameter must be measured in a separate experiment in the absence of the electroactive species.

A further disadvantage to the alternating-current method, especially when employed with solid electrodes, is that the double-layer capacity is frequency-dependent. However, as shown by Bockris and Conway,¹⁴¹ one may correct for this dispersion phenomenon. The vast superiority of the double-pulse galvanostatic method over all other methods, with the possible exception of the faradaic-rectification technique, is that one does not require a knowledge of the double-layer capacity. However, it must be pointed out that the theory assumes that the first current pulse only charges the double layer; i.e., it is entirely nonfaradaic. In actuality, the first current pulse is a step function and not a true pulse, which in theory should be represented by the Dirac or Kronecker delta function. Therefore, especially for extremely rapid electrode reactions, part of the initial current-step function may well be faradaic. It appears, therefore, that except for the most rapid reactions, the complexity of the instrumentation and the relative difficulty in interpreting the data preclude the double-pulse galvanostatic and faradaic-rectification methods in favor of the charge-step method. However, it must be pointed out that the alternating-current bridge methods are inherently more accurate than any perturbation-relaxation method involving the oscillographic recording of transients.

Delahay¹¹² has given a lucid, concise description of the experimental techniques necessary for application of most of the procedures discussed above. The original papers contain details concerning the merits and limitations of each method. The field of high-temperature electrochemistry in molten-salt media has received considerable attention in the last two decades. Although many experimental difficulties are associated with investigations in this type of medium, many of the limitations on the applicability of a particular procedure, due to the finite cell resistance, are less stringent because of the relatively high conductance of molten salts. A complete bibliography on the electrochemistry in molten salt media is contained in the general review by Reddy.¹⁴² Laitinen *et al.*^{143, 144} have reviewed the application of modern electrode-kinetic techniques in this medium.

A versatile potentiostat-galvanostat is an essential instrument in any electrochemical laboratory. Gerischer *et al.*,^{41, 145} Breiter and Will,¹⁴⁶ Fleischmann *et al.*,^{147, 148} and Will¹⁴⁹ have considered the important factors in the design of such instruments. One may maintain precision control over current and voltage by using either a voltage-feedback or an operational-feedback control circuit.¹⁵⁰ DeFord¹⁵¹ and Bard¹⁵² have discussed the use of solid-state operational amplifiers in potentiostat design. Several instruments utilizing solid-state circuitry have been designed.¹⁵¹⁻¹⁵⁷ An instrument employing a chopper-stabilized operational amplifier with negative feedback to amplify the error signal, the stable amplified signal then being used to drive a completely transistorized power amplifier, has been designed and constructed for use by the author¹⁵⁸ (see, also, Brown¹⁵⁶).

This general-purpose potentiostat-galvanostat has a rise time of 4×10^{-6} sec and a maximum current output of 10 Amp and controls potential to 1 mV. It has been successfully employed in the galvanostatic mode for a chronopotentiometric study in a molten-salt medium and will be described in a forthcoming publication.¹⁵⁹

XI. CONCLUSION

It is hoped that the author has been successful in his primary purpose, namely to acquaint the reader with the fundamental tenets of electrode kinetics and the methods whereby the characteristic parameters of rapid-charge transfer processes at electrode-electrolyte interfaces are evaluated. Purposely, electroanalytical methods, which have resulted from techniques originally aimed at elucidating electrode mechanisms, such as polarography and its many ramifications, have not been discussed. The monographs by Lingane³¹ and Delahay³³ contain details of these various techniques.

REFERENCES

1. D. J. G. Ives and G. J. Janz, Reference Electrodes, Academic Press, New York (1961).
2. Iu. K. Delimarskii and B. F. Markov, Electrochemistry of Fused Salts, Sigma Press, Washington, D. C., pp. 159 et seq. (1961).
3. J. O'M. Bockris, in Modern Aspects of Electrochemistry, No. 1., Ed. J. O'M. Bockris and B. E. Conway, Butterworths, London, p. 263 (1954).
4. R. Piontelli, Proc. 3rd C.I.T.C.E. meeting (Berne 1951), Manfredi, Milan (1952).
5. M. Eisenberg, C. W. Tobias, and C. R. Wilke, J. Electrochem. Soc. 102, 415 (1955).
6. E. Newbery, Trans. Far. Soc. 15, 126 (1919).
7. E. Newbery, J. Am. Chem. Soc. 42, 2007 (1920).
8. M. Knobel, P. Caplan, and M. Eiseman, Trans. Electrochem. Soc. 43, 56 (1923).
9. A. Hickling, Trans. Far. Soc. 33, 1540 (1937).
10. A. Hickling, J. Sci. Instrum. 15, 22 (1938).
11. D. Staicopoulos, E. Yeager, and F. Horvoka, J. Electrochem. Soc. 98, 68 (1951).
12. E. Yeager, T. Oey, and F. Horvoka, Tech. Report 6, O.N.R. contract 47002, Western Reserve Univ. (June 1952).
13. M. L. Kronenberg, J. C. Banter, E. Yeager, and F. Horvoka, J. Electrochem. Soc. 110, 1007 (1963).
14. E. J. Cairns and A. D. Tevebaugh, General Electric Research Laboratories, Schenectady, New York (private communication).
15. J. P. Elder and G. Wranglén, Electrochem. Tech. 2, 34 (1964).
16. N. Ibl, Electrochim. Acta 1, 3 (1959).
17. J. A. V. Butler, Trans. Far. Soc. 19, 729 (1923-24).
18. R. Parsons, *ibid*, 47, 1332 (1947).
19. D. C. Grahame, Chem. Revs. 41, 441 (1947).
20. R. Parsons, in Modern Aspects of Electrochemistry, No. 1, Ed. J. O'M Bockris, and B. E. Conway, Butterworths, London, Chap. 3 (1954).
21. R. Parsons, in Advances in Electrochemistry and Electrochemical Engineering, Vol. 1, Ed. P. Delahay and C. W. Tobias, Interscience, New York, Chap. 1 (1961).
22. N. F. Mott and R. J. Watts-Tobin, Electrochim. Acta. 4, 79 (1961).

23. J. Horiuti, J. Res. Inst. Cat. Hokkaido Univ., Sapporo, 1, 8 (1948).
24. A. Makrides, J. Electrochem. Soc. 104, 677 (1957).
25. H. Mauser, Z. Elektrochem. 62, 419 (1958).
26. D. M. Mohilner, J. Phys. Chem. 68, 623 (1964).
27. K. J. Vetter, Z. Elektrochem. 56, 931 (1952).
28. J. Tafel, Z. Physik. Chem. 50, 641 (1905).
29. J. P. Elder and A. Hickling, Trans. Far. Soc. 58, 1852 (1962).
30. A. Hickling, Trans. Far. Soc. 38, 27 (1942).
31. J. J. Lingane, Electroanalytical Chemistry, 2nd ed., Interscience, New York, Chap. 13, pp. 308-339 (1958).
32. I. M. Kolthoff and J. J. Lingane, Polarography, 2nd ed., Interscience, New York (1952).
33. P. Delahay, New Instrumental Methods in Electrochemistry, Interscience New York (1954).
34. L. Meites, Polarographic Techniques, Interscience, New York (1955).
35. S. Gilman, J. Phys. Chem. 66, 2657 (1962).
36. S. Gilman, *ibid*, 67, 78, 1898 (1963).
37. Z. Galus, H. Y. Lee, and R. N. Adams, J. Electroanal. Chem. 5, 17 (1963).
38. A. Fick, Pogg. Ann. 94, 59 (1855).
39. P. Delahay, J. Amer. Chem. Soc. 75, 1431 (1953).
40. H. Gerischer and W. Vielstich, Z. Physik. Chem. (Frankfurt) 3, 16 (1955).
41. H. Gerischer and W. Vielstich, *ibid*, 4, 10 (1955).
42. H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids, 2nd ed., Clarendon Press, Oxford, p. 485 (1959).
43. R. V. Churchill, Modern Operational Mathematics in Engineering, 1st ed., McGraw-Hill, New York (1944).
44. E. Jahnke and F. Emde, Tables of Functions, 4th ed., Dover, New York (1945).
45. W. Vielstich and P. Delahay, J. Amer. Chem. Soc. 79, 1874 (1957).
46. H. A. Laitinen, R. P. Tischer, and D. K. Roe, J. Electrochem. Soc. 107, 548 (1960).
47. F. P. Bowden and E. K. Rideal, Proc. Roy. Soc. (London) A120, 59 (1928).

48. A. Hickling *et al.*, Trans. Far. Soc. 41, 333 (1945); 42, 518 (1946); 43, 762 (1947); 44, 261 (1948); 46, 820 (1950); 57, 123 (1961).
49. A. N. Frumkin *et al.*, see reference 100 of our reference 3, p. 177.
50. J. A. V. Butler *et al.*, Proc. Roy. Soc. (London) A137, 604 (1932); A143, 89 (1933).
51. J. P. Elder, Electrochim. Acta 7, 417 (1962).
52. M. Breiter, C. A. Knorr, and W. Völkl, Z. Elektrochem. 59, 681 (1955).
53. J. P. Elder, Ph.D. thesis, Liverpool Univ., England (1961).
54. W. A. Roiter, W. A. Juza, and E. S. Polujan, Acta Physicochim. U.R.S.S. 10, 389, 845 (1939).
55. J. O'M. Bockris and E. C. Potter, J. Electrochem. Soc. 99, 169 (1952).
56. J. M. Matsen, *ibid*, 110, 222 (1963).
57. L. Karasyk, R. W. Law, and H. B. Linford, *ibid*, 111, 237 (1964).
58. T. P. Hoar, in Modern Aspects of Electrochemistry, No. 2, Ed. J. O'M. Bockris, Academic Press, New York, Chap. 4, p. 274 (1959).
59. P. Delahay and G. Mamantov, Anal. Chem. 27, 478 (1955).
60. H. F. Weber, Wied. Ann. Physik. 7, 536 (1879).
61. H. J. S. Sand, Phil. Mag. 1, 45 (1901).
62. T. R. Roseburgh and W. L. Miller, J. Phys. Chem. 14, 816 (1910).
63. Z. Karaoglanoff, Z. Elektrochem. 12, 5 (1906).
64. P. Delahay and T. Berzins, J. Amer. Chem. Soc. 75, 2486 (1953).
65. T. Berzins and P. Delahay, *ibid*, 75, 4205 (1953).
66. A. C. Testa and W. H. Reinmuth, Anal. Chem. 33, 1320 (1961).
67. W. H. Reinmuth, *ibid*, 33, 322 (1961).
68. P. Delahay, C. C. Mattax, and T. Berzins, J. Amer. Chem. Soc. 76, 5319 (1954).
69. J. A. V. Butler and G. Armstrong, Proc. Roy. Soc. (London) A139, 406 (1933).
70. L. Gierst and A. Juliard, J. Phys. Chem. 57, 701 (1953).
71. W. H. Reinmuth, Anal. Chem. 32, 1515 (1960).
72. A. C. Testa and W. H. Reinmuth, *ibid*, 33, 1324 (1961).
73. H. B. Herman and A. J. Bard, *ibid*, 35, 1121 (1963).
74. W. H. Reinmuth, *ibid*, 34, 1446 (1962).

75. R. W. Murray and C. N. Reilley, *J. Electroanal. Chem.* 3, 182 (1962).
76. T. Berzins and P. Delahay, *J. Chem. Phys.* 23, 972 (1955).
77. T. Berzins and P. Delahay, *Z. Elektrochem.* 59, 792 (1955).
78. T. Berzins and P. Delahay, *J. Amer. Chem. Soc.* 77, 6448 (1955).
79. H. Gerischer and M. Krause, *Z. Physik. Chem. (Frankfurt)* 10, 264 (1957).
80. H. Gerischer and M. Krause, *ibid*, 14, 184 (1958).
81. H. Matsuda, S. Oka, and P. Delahay, *J. Amer. Chem. Soc.* 81, 5077 (1959).
82. H. Matsuda and P. Delahay, *Coll. Czech. Chem. Comm.* 25, 2977 (1960).
83. W. H. Reinmuth and C. E. Wilson, *Anal. Chem.* 34, 1159 (1962).
84. G. C. Barker, in Transactions of the Symposium on Electrode Processes, Ed. E. Yeager, Philadelphia, May 1959, Wiley, New York, p. 325 (1961).
85. W. H. Reinmuth, *Anal. Chem.* 34, 1272 (1962).
86. P. Delahay, *J. Phys. Chem.* 66, 2204 (1962).
87. P. Delahay and A. Aramata, *ibid*, 66, 2208 (1962).
88. H. Gerischer, *Proc. 14th C.I.T.C.E. meeting (Rome, 1962)*.
89. P. Delahay, *J. Phys. Chem.* 67, 135 (1963).
90. P. Delahay, *Anal. Chem.* 34, 1267 (1962).
91. P. Delahay and Y. Ide, *ibid*, 34, 1580 (1962).
92. P. Delahay and Y. Ide, *ibid*, 35, 1119 (1963).
93. P. Delahay, *Review of Polarography (Japan)* 11, No. 1/2, 141 (1963).
94. P. Delahay, *Anal. Chim. Acta* 27, 400 (1962).
95. P. Delahay, *Anal. Chem.* 34, 1662 (1962).
96. P. Delahay and D. M. Mohilner, *J. Phys. Chem.* 66, 959 (1962).
97. P. Delahay and D. M. Mohilner, *J. Amer. Chem. Soc.* 84, 4247 (1962).
98. K. B. Oldham, *J. Electrochem. Soc.* 107, 766 (1960).
99. D. C. Grahame, *ibid*, 99, 370C (1952).
100. G. Falk and E. Lange, *Z. Elektrochem.* 54, 132 (1950).
101. H. Gerischer, *Z. Physik. Chem.* 198, 286 (1951).
102. H. Gerischer, *ibid*, 201, 55 (1952).

103. J. E. B. Randles, *Disc. Far. Soc.* 1, 11 (1947).
104. J. E. B. Randles and K. W. Somerton, *Trans. Far. Soc.* 48, 937, 951 (1952).
105. P. Dolin and B. V. Ershler, *Acta Physiochim. U.R.S.S.* 13, 747 (1940); 21, 213 (1946).
106. B. V. Ershler, *Disc. Far. Soc.* 1, 269 (1947).
107. B. V. Ershler, *Zhur. Fiz. Khim.* 22, 683 (1948).
108. D. C. Grahame, *J. Amer. Chem. Soc.* 68, 301 (1946).
109. E. Warburg, *Wied. Ann.* 67, 493 (1899).
110. E. Warburg, *Drud. Ann.* 6, 125 (1901).
111. F. Kruger, *Z. Physik. Chem.* 45, 1 (1903).
112. P. Delahay, in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 1, Ed. P. Delahay and C. W. Tobias, Interscience New York, pp. 271 et seq (1961).
113. M. Senda and P. Delahay, *J. Phys. Chem.* 65, 1580 (1961).
114. H-C. Chang and G. Jaffe', *J. Chem. Phys.* 20, 1071 (1952).
115. G. Jaffe', *Ann. Phys.* 16, 217, 249 (1933).
116. G. Jaffe' and J. A. Rider, *J. Chem. Phys.* 20, 1077 (1952).
117. A. Bewick and M. Fleischmann, *Ann. Reports Chem. Soc. (London)* 57, 92 (1960).
118. L. de Maeyer and K. Kustin, *Ann. Rev. Phys. Chem.* 14, 5 (1963).
119. M. Eigen and L. de Maeyer, in *Techniques of Organic Chemistry*, Vol. 8, Part 2, Ed. S. L. Friess, E. S. Lewis, and A. Weissberger, Wiley, New York, pp. 895 et seq (1963).
120. R. J. Brodd, *J. Res. Nat. Bur. Stand., A. Physics and Chemistry* 65, 275 (1961).
121. K. S. Cole and R. H. Cole, *J. Chem. Phys.* 9, 341 (1941).
122. R. J. Brodd and H. J. DeWane, *J. Electrochem. Soc.* 110, 1091 (1963).
123. C. J. F. Böttcher, *Theory of Electric Polarization*, Elsevier, New York, 1952, pp. 36 et seq.
124. H. Pellat, *Ann. Chim. Phys.* 18, 150, 571 (1899).
125. H. Pellat, *J. Physique*, 3rd series, 9, 313 (1900).
126. C. P. Symth, *Dielectric Behaviour and Structure*, McGraw-Hill, New York, Chap. 2, pp. 52 et seq (1955).

127. H. Fröhlich, Theory of Dielectrics, 2nd ed., Clarendon Press, Oxford, Chap. 3 (1958).
128. P. Debye, Polar Molecules, Dover, New York, Chap. 5, pp. 94 et seq (1945).
129. G. W. Vinal, Storage Batteries, 4th ed., Wiley, New York, pp. 326 et seq (1955).
130. K. S. G. Doss and H. P. Agarwal, J. Sci. Inst. Res. India 9B, 280 (1950).
131. K. B. Oldham, Trans. Far. Soc. 53, 80 (1957).
132. K. S. G. Doss and H. P. Agarwal, Proc. Indian Acad. Sci. 34A, 263 (1951).
133. K. S. G. Doss and H. P. Agarwal, *ibid*, 35A, 45 (1952).
134. G. C. Barker, Anal. Chim. Acta 18, 118 (1958).
135. G. C. Barker, R. L. Faircloth, and A. W. Gardner, Nature 181, 247 (1958).
136. Iu. A. Vdovin, Doklady Akad. Nauk S.S.S.R. 120, 554 (1958).
137. H. Matsuda and P. Delahay, J. Amer. Chem. Soc. 82, 1547 (1960).
138. P. Delahay, M. Senda, and C. H. Weiss, *ibid*, 83, 312 (1961).
139. M. Senda and P. Delahay, *ibid*, 83, 3763 (1961).
140. M. Senda, H. Imai, and P. Delahay, J. Phys. Chem. 65, 1253 (1961).
141. J. O'M. Bockris and B. E. Conway, J. Chem. Phys. 28, 707 (1958).
142. T. B. Reddy, Electrochem. Tech. 1, 325 (1963).
143. H. A. Laitinen and R. A. Osteryoung, in Fused Salts, Ed. B. R. Sundheim, McGraw-Hill, New York, Chap. 4 (1964).
144. C. H. Liu, K. E. Johnson, and H. A. Laitinen, in Molten Salt Chemistry, Ed. M. Blander, Interscience, New York, pp. 681-733 (1964).
145. H. Gerischer and K. E. Staubach, Z. Elektrochem. 61, 789 (1957).
146. M. Breiter and F. G. Will, *ibid*, 61, 1177 (1957).
147. M. Fleischmann, J. Sowerby, and H. R. Thirsk, Trans. Far. Soc. 53, 91 (1957).
148. A. Bewick, A. Bewick, M. Fleischmann, and M. Liler, Electrochim. Acta 1, 83 (1959).
149. F. G. Will, Z. Elektrochem. 63, 484, 689 (1959).

150. H. V. Malmstadt, C. G. Enke, and E. C. Toren, Jr., Electronics for Scientists, W. A. Benjamin, Inc., New York, Chap. 8, pp. 368 et seq (1963).
151. D. D. DeFord, Anal. Chem. 32, 31R (1960).
152. A. J. Bard, *ibid*, 34, 57R (1962).
153. G. L. Booman, *ibid*, 29, 213 (1957).
154. M. T. Kelley, H. C. Jones, and D. J. Fisher, *ibid*, 31, 488, 956 (1959).
155. J. E. Harrar, F. B. Stephens, and R. E. Pechacek, *ibid*, 34, 1036 (1962).
156. R. H. Brown, Report U.S.A.E.C.-I.D.O. 16852 (May 1963).
157. F. Lindstrom and J. B. Davis, Anal. Chem. 36, 11 (1964).
158. J. P. Elder, W. A. McDowell, and J. A. Plambeck, unpublished work.
159. J. P. Elder, J. A. Plambeck, and H. A. Laitinen, to be submitted for publication in J. Electrochem. Soc.