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## Faradaic Rectification and Electrode Processes

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A rather general theory of faradaic rectification is developed and previous theories are clarified and greatly extended. Theoretical results are substantiated by experiment. It is shown that two types of control must be considered simultaneously, namely, control of the mean and alternating components of the current or potential. In practice, the alternating current or potential is an essentially harmonic-free sinusoidal function of time, and either the mean current is equal to zero ( $I = 0$ ) or the mean potential is equal to the equilibrium potential ( $E = E_e$ ). The rectification voltage or the rectification current is the same regardless of control of the alternating component, and the second harmonic component of current or potential resulting from rectification is the same regardless of control of the mean component. A general equation is derived for the rectification voltage for control at  $I = 0$  without assumption about the form of the  $I$ - $E$  characteristic. Particular forms of this equation are derived in terms of the resistive and capacitive components of the series equivalent circuit for the faradaic impedance for a simple charge transfer process and a charge transfer process with preceding chemical reaction. The time-dependence of the rectification voltage is derived by consideration of the double layer charging without and with rectification from the double layer. Influence of the applied voltage, frequency and reactant concentrations is discussed. Methods for the calculation of the exchange current density and transfer coefficient are outlined without and with correction for the double layer structure. Limitations imposed by the circuit resistance are also discussed. It is shown from the general equation that the mean rectification current for control of  $E$  at  $E_e$  is the same as in the voltage-step potentiostatic method. The influence of the circuit resistance is readily accounted for. Apparatus is described for measurement of rectification voltages by application of a short single pulse (a few milliseconds or longer) of alternating voltage up to 2 megacycles per sec. Experimental results for discharge of mercurous ion in perchloric acid on mercury and for Ti(IV)-Ti(III) in tartaric acid medium at a dropping mercury electrode are given. It is concluded that the kinetic study of very fast reactions should still be feasible when other methods fail because interference by the double layer capacity is avoided and the influence of the cell resistance is greatly minimized.

### Introduction

The current-potential characteristic for electrode processes is linearized in the theory of the faradaic impedance and is assumed to be symmetrical with respect to the equilibrium potential  $E_e$ . Actually, current-potential curves are, in general, asymmetrical with respect to  $E_e$ , and there results *faradaic rectification*. This rectification effect can be applied to the study of electrode kinetics since it depends on the current-potential characteristic.

Faradaic rectification was discovered by Doss and Agarwal<sup>2a</sup> who designated it as "redoxokinetic" effect. The expression "faradaic rectification" was coined by Oldham.<sup>3</sup> Work on theory which is briefly covered below was done by Doss and Agarwal,<sup>2b</sup> Oldham,<sup>3</sup> Barker, Faircloth and Gardner,<sup>4</sup> Vdovin<sup>5</sup> and Matsuda and Delahay.<sup>6</sup> Application to electrode kinetics was discussed by these authors but Barker and co-workers<sup>4</sup> were the first to realize and fully demonstrate in an extensive experimental study the potentialities of faradaic rectification in the study of inherently fast electrode processes (*i.e.*, processes with a large exchange current density). The work of Fournier<sup>7</sup> who studied the distortion of polarographic waves upon superimposition of an alternating voltage is related to faradaic rectification. This author,

however, did not even allude to the possibility of application to electrode kinetics and limited herself to experimental observations. A sound basis for her observations was given by Tachi and co-workers,<sup>8</sup> but these authors did not consider faradaic rectification as discussed below. Application to kinetics was examined by Tachi and collaborators but for irreversible polarographic waves.

Control of mean electrical variables *versus* control of alternating variables was not clearly analyzed by previous authors and theory is in need of clarification. A rather general theory in which this and other questions not considered before is discussed here and substantiated by experimental work. These results were announced in a preliminary note.<sup>9</sup> A qualitative discussion, not previously reported, in which the matter of control is clarified will be presented first.

### Qualitative Discussion

**Types of Control.**—We consider an electrode process,  $O + ne = R$ , involving soluble species which has the current density-potential characteristic

$$I = I_a^0 \left\{ \frac{C_O}{C_O^0} \exp \left[ -\frac{\alpha n F}{RT} \eta \right] - \frac{C_R}{C_R^0} \exp \left[ \frac{(1 - \alpha) n F}{RT} \eta \right] \right\} \quad (1)$$

where  $I$  is the current density,  $C_O$  and  $C_R$  are the concentrations at the electrode,  $C_O^0$  and  $C_R^0$  are the bulk concentrations,  $I_a^0$  is the apparent (not corrected for double layer effects) exchange current density for the concentrations  $C_O^0$  and  $C_R^0$ ,  $\alpha$  is the transfer coefficient,  $\eta$  is the overvoltage ( $\eta = E - E_e$ ;  $E$  potential in the European convention at the current density  $I$ ,  $E_e$  equilibrium potential), and  $F$ ,  $R$ , and  $T$  have their usual significance. A net cathodic current is positive in eq. 1 and a net

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(2) (a) K. S. G. Doss and H. P. Agarwal, *J. Sci. Industr. Res. India*, **9B**, 280 (1950). (b) K. S. G. Doss and H. P. Agarwal, *Proc. India Acad. Sci.*, **34A**, 263 (1951); **35A**, 45 (1952).

(3) K. B. Oldham, *Trans. Faraday Soc.*, **53**, 80 (1957).

(4) (a) G. C. Barker, *Anal. Chim. Acta*, **18**, 118 (1958). (b) G. C. Barker, R. L. Faircloth and A. W. Gardner, *Nature*, **181**, 247 (1958). (c) G. C. Barker, "Transactions of the Symposium on Electrode Processes, Philadelphia, 1959," E. Yeager, editor, John Wiley and Sons, Inc., New York, N. Y., in course of publication.

(5) Iu. A. Vdovin, *Doklady Akad. Nauk S.S.S.R.*, **120**, 554 (1958).

(6) H. Matsuda and P. Delahay, *This Journal*, **82**, 1547 (1960).

(7) M. Fournier, *Comp. rend.*, **232**, 1673 (1951).

(8) M. Senda and I. Tachi, *Bull. Chem. Soc. Japan*, **28**, 632 (1955); see also four previous papers in this series.

(9) P. Delahay, M. Senda and C. H. Weis, *J. Phys. Chem.*, **64**, 960 (1960).

anodic current is negative. The kinetic parameter  $I_a^0$  can be written as<sup>10</sup>

$$I_a^0 = nFk_a^0 C_O^0 1 - \alpha C_R^0 \alpha \quad (2)$$

where  $k_a^0$  is the apparent standard rate constant. This equation holds provided that the concentrations of reactants in the pre-electrode state (*i.e.*, after correction for the double layer structure) are proportional to the concentrations outside the diffuse double layer.

In the faradaic rectification method, current and potential vary periodically and two types of control must be considered: (a) control of the *mean* component of the current density ( $\bar{I}$ ) or potential ( $\bar{E}$ ) and (b) control of the *alternating* component of the current density (*A.C. control*) or potential (*A.V. control*). If the alternating current is a harmonic-free sinusoidal function of time, the alternating component of the potential includes harmonics as a result of the asymmetry of the  $I-E$  curve about  $E_e$ . Conversely, the alternating component of the current contains harmonics when the alternating component of potential is free of harmonics.

Two particular cases of control of the mean component which are of interest,  $\bar{I} = 0$  and  $\bar{E} = E_e$ , will be discussed qualitatively for A.V. and A.C. control, the double layer capacity and circuit resistance being neglected. Complications resulting from the double layer capacity and cell resistance are discussed below in the quantitative treatment.

**Control of Mean Current Density to Zero.**—When there is A.C. control and  $\bar{I} = 0$ , the variations of  $E$  with time<sup>11</sup> are represented by the sum of a pure sinusoidal function at the same frequency  $f$  as the current and a periodic component at the frequency  $2f$  (Fig. 1A). The latter component results from the asymmetry of the  $I-E$  curve about  $E_e$ . The net result is a shift (toward anodic potentials in Fig. 1A) of the mean potential  $\bar{E}$  with respect to  $E_e$ , *i.e.*, there appears a *rectification voltage*  $\bar{E} - E_e$ . Since  $\bar{I} = 0$ , there is no net chemical change and there is no mass transfer polarization for the mean components of the concentrations. Hence, the mean rectification voltage is time-independent when the double layer is neglected. When the alternating current is interrupted, the rectification voltage drops to zero immediately.

Rectification for  $\bar{I} = 0$  and A.V. control results in an alternating current component of frequency  $2f$  (Fig. 1B). This current component must be compensated since  $\bar{I} = 0$ . Further, the alternating component of the potential must be free of harmonics because of A.V. control. The alternating component of the current at the frequency  $2f$  must therefore be compensated on a time average by an equivalent current of constant amplitude and opposite direction. This compensation requires the mean potential to shift with respect to  $E_e$  (toward anodic potentials in Fig. 1B) and there appears

(10) For a recent review, see Chapter 5 by P. Delahay in "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and C. W. Tobias, editors, Interscience Publishing Co., New York, N. Y., in course of publication.

(11) The alternating component cannot be determined by direct reading on the  $I-E$  characteristic of the current corresponding to a given departure of potential from  $E_e$  except in the limiting case of an infinite frequency. Mass transfer must be considered at finite frequencies, and the sinusoidal components of  $I$  and  $E$  are not in phase. It will be assumed here that the frequency is infinite.

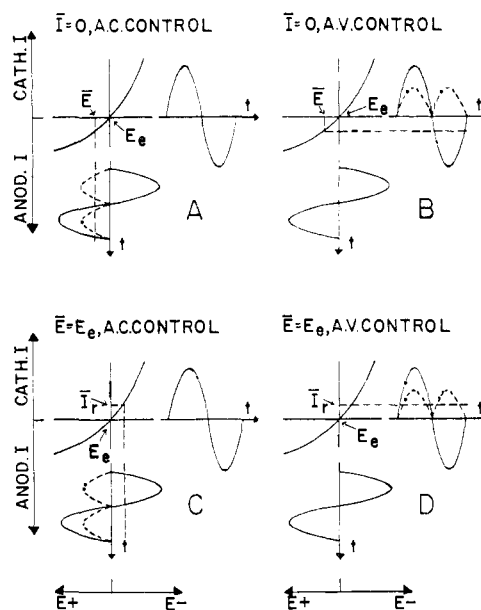


Fig. 1.—Diagram of the qualitative discussion of faradaic rectification.

a rectification voltage  $\bar{E} - E_e$ . Since  $\bar{I} = 0$ , the mean rectification voltage is time-independent if the double layer is not considered, just as for  $\bar{I} = 0$  and A. C. control. Finally, the rectification voltage is the same whether there is A.C. or A.V. control because of the reciprocity relationship between Figs. 1A and B.

**Control of the Mean Potential at the Equilibrium Potential.**—Rectification for  $\bar{E} = E_e$  and A.C. control results in an alternating component of potential at the frequency  $2f$  (Fig. 1C) which must be compensated since  $\bar{E} = E_e$ . Further, the alternating current must be harmonic-free because of A.C. control. The frequency  $2f$  component of the potential therefore must be compensated on a time average by an equivalent shift of potential of constant amplitude and opposite direction. Compensation thus results in a net *rectification current*  $I_r$ .

The rectification current is accompanied by a net chemical change. Reactant concentrations change at the electrode, and  $E_e$  drifts as  $t \rightarrow \infty$  (toward cathodic potentials for Fig. 1C) toward a limiting value  $E_e'$  about which the  $I-E$  curve is symmetrical. Rectification vanishes for  $t \rightarrow \infty$ . The necessary experimental conditions, however, should prove difficult to achieve since  $\bar{E}$  must be maintained at the varying equilibrium potential  $E_e$  and a low resistance path must be provided for the rectification current. A solution is to compensate exactly the mean rectification current by a current of opposite direction from an external source, when the alternating current is applied, so that  $E_e$  remains unchanged. Faradaic rectification is then studied from measurement of this compensating current.

A.V. control for  $\bar{E} = E_e$  results in current-time variations equivalent to a sine wave of frequency  $f$  and a periodic component of frequency  $2f$  (Fig. 1D). The latter is equivalent to a mean rectification current which has the same magnitude and direction as for A.C. control (Fig. 1C). The best experi-

mental procedure is to compensate the rectification current to achieve constant  $E_e$  just as for A.C. control.

To summarize the previous analysis: control of  $\bar{I}$  at zero results in the same rectification voltage whether there is A.C. or A.V. control; control of  $\bar{E}$  at  $E_e$  results in a rectification current  $\bar{I}_r$  which is independent of the type of control of the alternating component. Further, the component at the frequency  $2f$  appears in the potential when there is A.C. control and in the current when there is A.V. control. The type of alternating component control is thus immaterial as far as the rectification voltage or current are concerned, and only the control of the mean component of current or potential must be considered. Conversely, the control of the mean component of current or potential is immaterial for the frequency  $2f$  component, and only the type of alternating component control need be considered.

Apparatus for  $\bar{I} = 0$  control must be such that the direct current resistance of the circuit across the cell be, in principle, infinite, *i.e.*, the cell must be connected to the alternating current generator through a leak-free capacitor.

### Rectification Voltage and Mean Rectification Current Density

**General Correlations.**—Non-linearity of the  $I$ - $E$  characteristic about  $E_e$  for  $|\eta| \ll RT/\alpha nF$  can be taken into account by inclusion of the terms in  $\eta^2$  in the expansion of eq. 1. The resulting equation has been used by most investigators as the basis for analysis of faradaic rectification just as the linearized form of eq. 1 is applied in the treatment of faradaic impedance and other relaxation methods<sup>10</sup> (except the potential-step method). A more general treatment in which a particular form of the  $I$ - $E$  equation is not postulated at the onset is desirable for faradaic rectification, as will be noted below, and in fact was developed by Grahame<sup>12</sup> for the faradaic impedance method.

The linearized  $I$ - $E$  equation for a small departure from equilibrium

$$((nF/RT)\delta E \ll 1, |\delta C_O/C_O^0| \ll 1, |\delta C_R^0/C_R^0| \ll 1)$$

is written quite generally as

$$\delta I = ((\delta I/\delta E)\delta E + (\partial I/\partial C_O)\delta C_O + (\partial I/\partial C_R)\delta C_R$$

where  $\delta$  represents a variation of the quantity being considered and the partial derivatives are expressed at the equilibrium potential  $E_e$ . The variations  $\delta C_O$  and  $\delta C_R$  can be expressed in terms of the resistive and capacitive elements of the equivalent circuit of the faradaic impedance, and a general equation is obtained for the faradaic impedance in terms of these elements and the charge transfer resistance per unit area,<sup>13</sup>  $r_{ct} = -(\partial\eta/\partial I)_{I \rightarrow 0} = (RT/nF)(1/I_e^0)$ . Particular forms of the faradaic impedance are derived by introduction of the values of  $\partial I/\partial E$ ,  $\partial I/\partial C_O$  and  $\partial I/\partial C_R$  corresponding to the  $I$ - $E$  characteristic being selected. Such an ap-

proach has no particular advantage in the treatment of the faradaic impedance, except perhaps its elegance, over the more direct analysis based on the linearized form of eq. 1. There is, however, an advantage for faradaic rectification, namely that this approach brings out general relationships, useful to the understanding of the method, which otherwise might be hidden by the complexity of algebra. This general treatment is developed below, and correlation is made with results obtained by other investigators. The double layer capacity and cell resistance are neglected at first but are considered afterward.

We express at the onset  $\delta I$  in terms of  $\delta E$ ,  $\delta C_O$  and  $\delta C_R$  as for the faradaic impedance, but we now include the second partial derivatives of the function  $I = f(E, C_O, C_R)$  to take into account the non-linearity of the  $I$ - $E$  curve about  $E_e$ . We further note that  $\delta I = \sum_{p=0}^2 \delta_p I$  where  $p = 0, 1$  and  $2$  corresponds, respectively, to the mean value of  $I$ , the fundamental frequency term, and the second harmonic term. Higher harmonics are neglected since only a small departure from equilibrium is considered. The mean value corresponds to steady state for the alternating component, *i.e.*, for  $(\omega t)^{1/2} \gg 1$  ( $\omega = 2\pi f$ ). We write for  $\delta_p I$

$$\delta_p I = \frac{\partial I}{\partial E} \delta_p E + \frac{\partial I}{\partial C_O} \delta_p C_O + \frac{\partial I}{\partial C_R} \delta_p C_R + \delta_p^2 I \quad (3)$$

where the correction for non-linearity  $\delta_p^2 I$  is

$$\delta_p^2 I \approx \frac{1}{2} \left\{ \frac{\partial^2 I}{\partial E^2} [(\delta_1 E)^2]_p + \frac{\partial^2 I}{\partial C_O^2} [(\delta_1 C_O)^2]_p + \frac{\partial^2 I}{\partial C_R^2} [(\delta_1 C_R)^2]_p \right\} + \left\{ \frac{\partial^2 I}{\partial E \partial C_O} [\delta_1 E \delta_1 C_O]_p + \frac{\partial^2 I}{\partial E \partial C_R} [\delta_1 E \delta_1 C_R]_p + \frac{\partial^2 I}{\partial C_O \partial C_R} [\delta_1 C_O \delta_1 C_R]_p \right\} \quad (4)$$

for  $p = 0$  and  $p = 2$ . One has  $\delta_p^2 I = 0$  for  $p = 1$ , since  $p = 1$  corresponds to the linearized  $I$ - $E$  curve. Equation 4 is approximate because the  $p$ -values of  $(\delta_1 E)^2$  and other terms are taken rather than the  $p$ -values of  $\delta E$ ,  $\delta C_O$  and  $\delta C_R$ . This approximation is entirely justified since  $\delta_1 E \gg \delta_0 E$ ,  $\delta_1 E \gg \delta_2 E$ ,  $\delta_1 C_O \gg \delta_0 C_O$ ,  $\delta_1 C_O \gg \delta_2 C_O$ ,  $\delta_1 C_R \gg \delta_0 C_R$ ,  $\delta_1 C_R \gg \delta_2 C_R$ .

One of the mean component  $\delta_0 I$  or  $\delta_0 E$  can be controlled, and one generally selects either  $\delta_0 I = 0$  (mean current equal to zero) or  $\delta_0 E = 0$  (mean potential equal to the equilibrium potential). If  $\delta_0 I = 0$ , there is no net change in the mean concentrations of substances O and R, and consequently  $\delta_0 C_O \equiv \delta_0 C_R \equiv 0$  independently of the control of the alternating component (A.C. or A.V. control). One then deduces from eq. 3

$$\delta_0 E = -\frac{\delta_0^2 I}{\partial E} \quad (5)$$

where  $-1/(\partial I/\partial E)$  is the charge transfer resistance.<sup>13</sup> Since there is no net change in the mean concentrations of O and R,  $\delta_0 E$  should be independent of time at least if the double layer capacity is not considered.

If  $\delta_0 E = 0$ , the mean rectification current density is given by eq. 3 as written for  $p = 0$  in which the term in  $\delta_0 E$  vanishes. The value of  $\delta_0 I$  can be ex-

(12) (a) D. C. Grahame, *J. Electrochem. Soc.*, **99**, C 370 (1952).  
(b) For a summary, see P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishing Co., New York, N. Y., 1954, pp. 148-159.

(13) The electrode behaves as the resistance  $r_{ct}$  and follows Ohm's law in the absence of mass transfer polarization ( $C_O = C_O^0$ ,  $C_R = C_R^0$ ) when  $|\eta| \ll RT/\alpha nF$ .

pressed in terms of the shift of mean potential obtained in the method with control of  $\delta_0 I$  at zero by combination of eq. 3 and 5. Thus

$$\delta_0 I = -\frac{\partial I}{\partial E} \delta_0 E + \frac{\partial I}{\partial C_O} \delta_0 C_O + \frac{\partial I}{\partial C_R} \delta_0 C_R \quad (6)$$

The mean rectification current is the same as the current which would be observed in the potentiostatic method for a potential step  $-\delta_0 E$ . The result derived by Gerischer and Vielstich<sup>14</sup> for the current density in the potentiostatic method, as written for the linearized  $I-E$  characteristic, thus applies here

$$I_r = \delta_0 E \frac{nF}{RT} I_a^0 \exp(\lambda^2 t) \operatorname{erfc}(\lambda t^{1/2}) \quad (7)$$

with

$$\lambda = \frac{I_a^0}{nF} \left( \frac{1}{C_O^0 D_O^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \quad (8)$$

The time-independent factors in eq. 7 represent the value of  $I$  at  $t = 0$ , *i.e.*, the value of  $I$  one calculates for  $\eta = -\delta_0 E$ . The time-dependent factors represent the effect of increasing mass transfer polarization ( $\exp(\lambda^2 t) \operatorname{erfc}(\lambda t^{1/2}) \rightarrow 0$  for  $t \rightarrow \infty$ ).

**Second Harmonic Terms.**—Second harmonic terms are also readily analyzed on the basis of eq. 3. When there is A.C. control, the current is free of harmonics, *i.e.*,  $\delta_2 I = 0$ , and consequently  $\delta_2 C_O \equiv \delta_2 C_R \equiv 0$ . Hence eq. 5, as written in terms of  $\delta_2 E$  and  $\delta_2^2 I$ , holds independently of the control of the mean component. Conversely,  $\delta_2 E = 0$  for A.V. control, and eq. 6, as written in terms of  $\delta_2 I$ ,  $\delta_2 E$ ,  $\delta_2 C_O$  and  $\delta_2 C_R$ , gives the variations of current for the second harmonic. This equation is the same as eq. 3 as written for  $p=1$  ( $\delta_1^2 I = 0$ ), for the fundamental frequency, except for the sign of  $\delta_2 E$ . Consequently, formulas for elements of the equivalent circuit for the second harmonic are the same as for the fundamental frequency (see eq. 10, 11 and 22 below) except that  $2\omega$  is substituted for  $\omega$ , and  $\delta_2 I$  is the current corresponding to the application of  $-\delta_2 E$  to the equivalent circuit.

Theory of the second harmonic terms for the faradaic impedance is thus available without further work. Measurements of second harmonic terms might be of limited interest in analytical applications as noted by Bauer.<sup>15</sup> Interference from the double layer capacity is minimized for second harmonic terms because rectification due to the double layer capacity (as a result of the non-linearity of the charge on the electrode versus potential relationship) is in general smaller than for the charge transfer reaction. Bauer's suggestion could be extended to application of the faradaic impedance method to fast reactions but the limitation imposed by the cell resistance is the same for the fundamental frequency and the second harmonic terms. Further, measurement of second harmonic terms requires a generator whose output is essentially free of the second harmonic.

**General Equation for the Rectification Voltage.**—Application of eq. 5 requires the derivation of the explicit form of the quantity  $\delta_0^2 I$  defined by eq. 4. The partial derivatives at  $E_0$  in the latter equation are readily written from the  $I-E$  characteristic, and only the  $\delta$ 's must be derived. It is to be noted that the terms in  $\partial^2 I / \partial C_O^2$ ,  $\partial^2 I / \partial C_R^2$  and  $\partial^2 I / \partial C_O \partial C_R$  vanish when the  $I-E$  characteristic is of the first order with respect to  $C_O$  and  $C_R$  since these derivatives are then equal to zero. The quantities  $\delta_0 E$ ,  $\delta_0 C_O$  and  $\delta_0 C_R$  can be expressed in terms of elements of the equivalent circuit for the electrode reaction as shown in Appendix. If the  $I-E$  characteristic of eq. 1 holds, the rectification voltage

(14) H. Gerischer and W. Vielstich, *Z. physik. Chem. (Frankfurt)*, **3**, 16 (1955).

(15) H. H. Bauer, *J. Electroanal. Chem.*, **1**, 256 (1960).

$\Delta \bar{E}_\infty$  ( $\equiv \delta_0 E$ ) is

$$\Delta \bar{E}_\infty = \frac{nF}{RT} V_A^2 \left\{ \frac{2\alpha - 1}{4} + \frac{r_s [(1 - \alpha)r_R - \alpha r_O] + y_s [(1 - \alpha)y_R - \alpha y_O]}{2(r_s^2 + y_s^2)} \right\} \quad (9)$$

where  $r_s$  and  $y_s$  are the real (resistive) and imaginary (capacitive) components of the series equivalent circuit for the total faradaic impedance per unit area  $Z$  ( $Z = r_F - jy_F$ , with  $j = (-1)^{1/2}$ ); and  $r_O$ ,  $r_R$ ,  $y_O$ ,  $y_R$  are the corresponding components for substances O and R for that part of the impedance corresponding to supply and removal of reactants by diffusion and possibly a heterogeneous or homogeneous chemical reaction. It is assumed in the case of a coupled chemical reaction that the kinetic parameters for this reaction can be regarded as potential-independent in the interval of potentials being considered. We use the symbol  $\Delta \bar{E}_\infty$  because  $\Delta \bar{E}$  is a function of time when the double layer capacity is considered (see below) and the above value corresponds to  $t \rightarrow \infty$ . One has

$$r_s = r_{ct} + r_O + r_R \quad (10)$$

$$y_s = y_O + y_R \quad (11)$$

$r_{ct}$  being the charge transfer resistance per unit area.<sup>13</sup> Values of the  $r$ 's and  $y$ 's in eq. 9 can be taken directly from the classical theory of faradaic impedance.

Equation 9 reduces to the result derived by Doss and Agarwal,<sup>2b</sup> Barker, Faircloth and Gardner<sup>4b</sup> and Vdovin<sup>5</sup> for a simple charge transfer reaction. These authors did not write their results in the general form of eq. 9 but used the rate constant at the equilibrium potential (not the apparent standard rate constant). They assumed that the current density is  $I_A \sin \omega t$  and thus postulated *implicitly* that the mean current is equal to zero. They wrote the potential as  $E_0 + \Delta \bar{E}_\infty - V_A \sin(\omega t - \theta_a)$  where  $\Delta \bar{E}_\infty$  is the rectification voltage and the minus sign for  $V_A \sin(\omega t - \theta_a)$  results from the convention of considering a cathodic current as positive. They finally introduced in eq. 1 these values of the current density and  $E$  and the values of the concentrations and  $\theta_a$  taken from the classical theory of the faradaic impedance and expanded the exponentials, the expansion being limited to the first three terms. The resulting equation was solved for  $\Delta \bar{E}_\infty$ .

The mean rectification current was derived by Matsuda and Delahay<sup>6</sup> before the general considerations which lead to eq. 6 had been put forward. They correlated the concentrations in eq. 1 for the  $I-E$  characteristic to the current density by<sup>16</sup>

$$C_i = C_i^0 \mp \frac{1}{\pi^{1/2} D_i^{1/2}} \int_0^t \frac{I(u)}{nF(t-u)^{1/2}} du \quad (12)$$

where the current density  $I(t)$  is some function of time and  $u$  is the integration variable. The  $\mp$  sign corresponds to substances O and R, respectively. The potential in eq. 1 for the  $I-E$  characteristic was set as  $E_0 - V_A \sin \omega t$ , and it thus was *implicitly* assumed that the mean potential is controlled at  $E_0$ . There resulted an integral equation in  $I(t)$  which was solved by expansion in series of the exponentials. Expansion, limited to the first degree terms, yielded two integral equations whose solution corresponded to the classical theory of faradaic impedance. Consideration of an additional term in the expansion yielded another integral equation whose solution gave an equation identical to eq. 7 ( $\delta_0 E \equiv \Delta \bar{E}_\infty$ ).

It is to be noted that a clear distinction between the two types of control, namely, simultaneous control of one of the mean components and one of the alternating components of the electrical variables was not made by these various investigators.

(16) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947, p. 57, eq. 9.

### Influence of the Double Layer Capacity for Control of $\bar{I}$ at Zero

**No Rectification from the Double Layer.**—Variation of the charge of the double layer was neglected above, and it was assumed that  $\bar{I} = 0$  for the faradaic process, whereas actually the total current density is controlled at zero. The previous analysis must be modified accordingly.

It will be assumed first that the differential capacity of the double layer  $c_1$  is independent of potential for a small departure from  $E_e$ , i.e., rectification due to the non-linearity of the charge-potential relationship for the double layer will be neglected at first. It will also be assumed that  $c_1$  is solely determined by the supporting electrolyte and is not affected by variations of  $C_0$  and  $C_R$ .

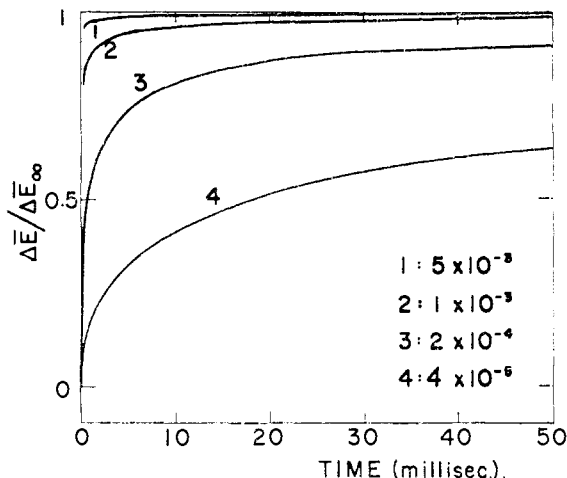


Fig. 2.—Plot of  $\Delta\bar{E}/\Delta\bar{E}_\infty$  against time for different total concentrations  $C_0^0 + C_R^0$  (expressed as the parameter  $n^2(C_0^0 + C_R^0)$  where the  $C^0$ 's are in mole l.<sup>-1</sup>) and for  $C_0^0/C_R^0 = 1$ ,  $k_a^0 = 1$  cm. sec.<sup>-1</sup>,  $D_0 = D_R = 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>,  $c_1 = 20$  microfarads cm.<sup>-2</sup>

The variation of the mean component of the charge  $q$  on the electrode is  $\delta_0 q = (dq/dE)\delta_0 E$  or  $\delta_0 q = c_1 \delta_0 E$ . One also has  $\delta_0 q = \int_0^t \delta_0 I dt$  where  $\delta_0 I$  is the varying mean current supplied by the charge transfer reaction for charging of the double layer over the interval  $\delta_0 E$ . The mean charging current is such that (see eq. 3 and 5)

$$\delta_0 I = \frac{1}{c_1} \left[ \int_0^t \delta_0 I dt - \Delta\bar{E}_\infty \right] \frac{\partial I}{\partial \bar{E}} + \frac{\partial I}{\partial C_0} \delta_0 C_0 + \frac{\partial I}{\partial C_R} \delta_0 C_R \quad (13)$$

The changes in concentrations  $\delta_0 C_0$  and  $\delta_0 C_R$  can be correlated to the current density by eq. 12, and an equation is obtained which can be solved for  $\delta_0 I$ . Since  $\int_0^t \delta_0 I dt = c_1 \delta_0 E$  the mean rectification voltage  $\Delta\bar{E}$  ( $\equiv \delta_0 E$ ) is obtained by integration of  $\delta_0 I$ . There follows after substitution of  $\partial I/\partial \bar{E}$ ,  $\partial I/\partial C_0$  and  $\partial I/\partial C_R$  by the corresponding values deduced from eq. 1

$$\Delta\bar{E} = \Delta\bar{E}_\infty \left\{ 1 - \frac{1}{c_1} \frac{I_a^0 nF}{RT} \frac{1}{H} \left[ \frac{1}{G} \exp(G^2 t) \operatorname{erfc}(Gt^{1/2}) - \frac{1}{H} \exp(H^2 t) \operatorname{erfc}(Ht^{1/2}) \right] \right\} \quad (14)$$

where  $\Delta\bar{E}_\infty$  is given by eq. 9 and

$$G, H = \frac{1}{2} \left\{ \frac{I_a^0}{nF} \left( \frac{1}{C_0^0 D_0^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \pm \left[ \left( \frac{I_a^0}{nF} \left( \frac{1}{C_0^0 D_0^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \right)^2 - 4I_a^0 \frac{nF}{RT} \frac{1}{c_1} \right]^{1/2} \right\} \quad (15)$$

One can show from eq. 14 that  $\Delta\bar{E} = 0$  for  $t = 0$  and  $\Delta\bar{E} \rightarrow \Delta\bar{E}_\infty$  for  $t \rightarrow \infty$  (Fig. 2). Mass transfer polarization for the mean concentrations  $C_0$  and  $C_R$  thus vanishes progressively, and the value  $\Delta\bar{E}_\infty$ , as calculated for  $\bar{I} = 0$ , is ultimately attained. Further, variations of  $\Delta\bar{E}/\Delta\bar{E}_\infty$  with time are not affected by frequency. One also can show that  $\Delta\bar{E} = \Delta\bar{E}_\infty$  for  $t > 0$  when  $c_1 = 0$  and that  $\Delta\bar{E} = 0$  for  $t \geq 0$  when  $c_1 \rightarrow \infty$ . Further, one deduces from eq. 14 after expansion of the error functions that  $\Delta\bar{E}$  varies linearly with  $1/t^{1/2}$  for large arguments, namely

$$\Delta\bar{E} = \Delta\bar{E}_\infty \left[ 1 - \frac{RT}{(nF)^2} c_1 \left( \frac{1}{C_0^0 D_0^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \frac{1}{(\pi t)^{1/2}} \right] \quad (16)$$

The lowest values of  $t$  for which this approximation holds decrease with an increasing apparent standard rate constant  $k_a^0$  for given  $C^0$ 's; and the limiting value  $\Delta\bar{E}_\infty$  is practically reached in a short time (perhaps a few milliseconds) for inherently fast reaction and sufficiently concentrated solutions. The time dependence of  $\Delta\bar{E}$  for a given reaction and a given  $C_0^0 + C_R^0$  also depends on the ratio  $C_0^0/C_R^0$  as one would expect from the form of the parameters  $G$  and  $H$  of eq. 15. Likewise,  $\Delta\bar{E}/\Delta\bar{E}_\infty$  depends on  $C_0^0 + C_R^0$  for a given  $C_0^0/C_R^0$  all other conditions being identical (Fig. 2).

The foregoing analysis also holds for the decay curve for  $\Delta\bar{E}$  when the alternating current is interrupted after the limiting value  $\Delta\bar{E}_\infty$  is practically attained. The right-hand member of eq. 14 is now equal to  $\Delta\bar{E}_\infty - \Delta\bar{E}$ . This conclusion holds only when  $\Delta\bar{E}_\infty$  is reached at the time of interruption since the previous analysis presupposes no mass transfer polarization for the mean concentrations before variation of the alternating current.

The foregoing conclusion that  $\Delta\bar{E}/\Delta\bar{E}_\infty$  is independent of  $V_A^2$  is strikingly verified in Fig. 3 for the Ti(IV)-Ti(III) charge transfer process.<sup>17</sup> The shape of the  $\Delta\bar{E}$  against  $t$  curve was not altered when  $\Delta\bar{E}_\infty$  varied in the ratio 1 to 20. Further, the decay curves have the same shape as the build-up curves (upside down). Note the effect of noise at the highest sensitivity. Verification of the frequency-independence of  $\Delta\bar{E}/\Delta\bar{E}_\infty$  against  $t$  is given in Fig. 4 for the discharge of Hg(I) on mercury.<sup>18</sup>

The influence of the concentrations  $C_0^0$  and  $C_R^0$  on the  $\Delta\bar{E}/\Delta\bar{E}_\infty$  against  $t$  curve is shown in Fig. 5 for the Ti(IV)-Ti(III) couple. Note that  $\Delta\bar{E}_\infty$  is approached more slowly when  $(1/C_0^0 D_0^{1/2}) + (1/C_R^0 D_R^{1/2})$  increases as one would expect from eq. 14 (see its simplified form in eq. 16 which is however not applicable here in all rigor).

(17) For a faradaic impedance study of this couple, see J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937 (1952).

(18) For studies of this process by the double pulse galvanostatic method, see H. Gerischer and M. Krause, *Z. physik. Chem. (Frankfurt)*, **14**, 184 (1958); H. Matsuda, S. Oka and P. Delahay, *THIS JOURNAL*, **81**, 5077 (1959).

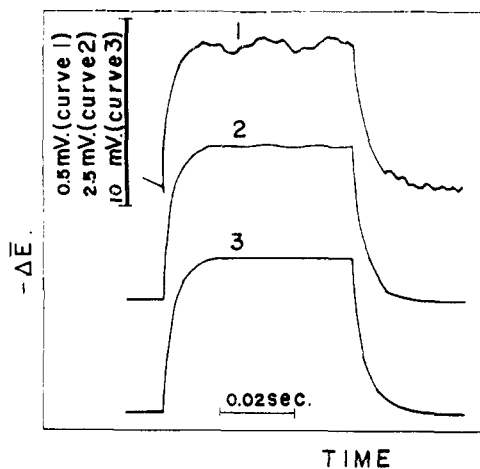


Fig. 3.—Tracings of oscillograms of  $\Delta\bar{E}$  versus  $t$  for 1.4 mM Ti(IV) plus 18.1 mM Ti(III) in 0.88 M  $\text{H}_2\text{SO}_4$ , 0.5 M tartaric acid for different applied voltages  $V_A$ . Ripples are due to hum and noise.

**Rectification from the Double Layer.**—The foregoing treatment will now be modified to take into account rectification due to the double layer. As was shown by Barker,<sup>4c</sup> variations of the differential capacity  $c_1$  of the double layer with potential results in a shift of the mean potential

$$\Delta E_i = -\frac{1}{4c_1} \frac{dc_1}{dE} V_A^2 \quad (17)$$

when the mean non-faradaic current is equal to zero. There  $V_A$  is the amplitude of the alternating voltage across  $c_1$ . The shift  $\Delta E_i$  is frequency independent if  $(1/c_1)(dc_1/dE)$  does not depend on frequency. This seems to be so for the mercury electrode at frequencies studied thus far, *i.e.*, up to 1–2 megacycles per sec. for the electrolytes studied by Barker.<sup>4c</sup>

If there is a charge transfer reaction, the net shift of mean potential is a combination of the shift of potential of eq. 14 and  $\Delta E_i$  of eq. 17. The term between brackets in eq. 13 now includes  $\Delta E_i$ , and eq. 14 is replaced by

$$\Delta\bar{E} = \Delta\bar{E}_\infty - (\Delta\bar{E}_\infty - \Delta\bar{E}_i) \frac{1}{c_1} I_a^0 \frac{nF}{RT} \frac{1}{H-G} \left[ \frac{1}{G} \exp(Gt) \operatorname{erfc}(Gt^{1/2}) - \frac{1}{H} \exp(Ht) \operatorname{erfc}(Ht^{1/2}) \right] \quad (18)$$

It follows from eq. 18 that  $\Delta\bar{E} = \Delta\bar{E}_i$  at  $t = 0$ , and  $\Delta\bar{E} = \Delta\bar{E}_\infty$  for  $t \rightarrow \infty$ . The shift of mean potential upon interruption of the alternating current when  $\Delta\bar{E}_\infty$  is practically reached is  $-\Delta\bar{E}_i$ . These conclusions from theory are borne out experimentally (Fig. 4).  $\Delta\bar{E}_i$  and  $\Delta\bar{E}_\infty$  may have the same or opposite signs.

**Influence of Circuit Resistance for Control of  $\bar{E}$  at  $E_a$ .**—The analysis is similar to the treatment of the potentiostatic voltage-step method given by Vielstich and Delahay.<sup>19</sup> We now include the ohmic drop  $r\delta_0 I$  ( $r$  total resistance of cell and circuit for the measurement of  $I_r$ ) in writing eq. 6, *i.e.*

$$\delta_0 I = \frac{\partial I}{\partial E} (-\Delta\bar{E}_\infty + r\delta_0 I) + \frac{\partial I}{\partial C_0} \delta_0 C_0 + \frac{\partial I}{\partial C_R} \delta_0 C_R \quad (19)$$

(19) W. Vielstich and P. Delahay, *THIS JOURNAL*, **79**, 1874 (1957)

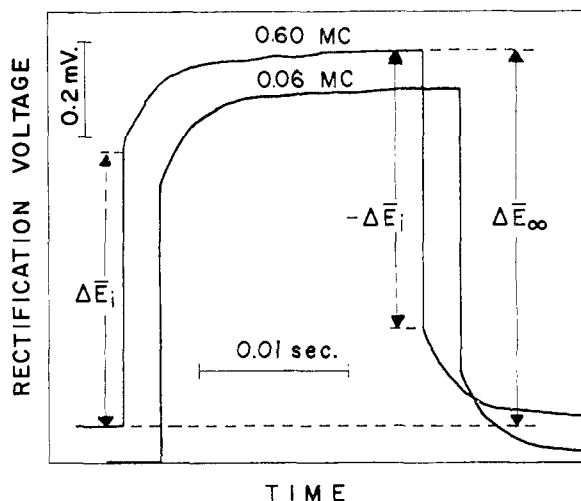


Fig. 4.—Tracings of oscillograms of  $\Delta\bar{E}$  against  $t$  for discharge of 0.08 mM Hg(I) in 1.14 M  $\text{HClO}_4$  for two frequencies. Ripples are due to hum and noise.

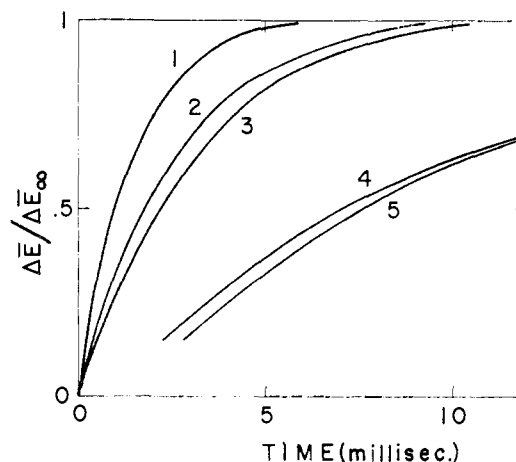


Fig. 5.—Tracings of oscillograms of  $\Delta\bar{E}/\Delta\bar{E}_\infty$  against  $t$  for Ti(IV)-Ti(III) in 0.88 M  $\text{H}_2\text{SO}_4$  and 0.5 M tartaric acid. Concentrations for curves 1 to 5: 6.2, 17.4, 1.3, 0.61, and 1.4 mM Ti(IV); 13.3, 2.1, 18.2, 1.35, and 0.55 mM Ti(III). Values of  $(1/C_0^0 D_0^{1/2}) + (1/C_R^0 D_R^{1/2})$  in  $10^8 \text{ sec.}^{1/2} \text{ mole}^{-1} \text{ cm.}^2$  for curves 1 to 5: 1.1, 2.8, 4.0, 11.4, 12.0 for  $D_{\text{Ti(IV)}} = D_{\text{Ti(III)}} = 0.44 \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1}$   $\Delta\bar{E}$  and  $\Delta\bar{E}_\infty$  were positive for curve 2 and negative for the other curves. Ripples due to hum and noise not represented.

The mean rectification current density is

$$I_r = \frac{\Delta\bar{E}_\infty}{r + \frac{1}{I_a^0} \frac{RT}{nF}} \exp(\lambda'^2 t) \operatorname{erfc}(\lambda' t^{1/2}) \quad (20)$$

with

$$\lambda' = \frac{1}{nF \left( \frac{1}{I_a^0} + \frac{nF}{RT} r \right)} \left( \frac{1}{C_0^0 D_0^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \quad (21)$$

and previous discussion<sup>19</sup> of this result applies here.  $I_r$  is primarily determined by the circuit resistance  $r$  and not by the kinetics of the charge transfer reaction when  $r$  is appreciably larger than the charge transfer resistance  $(RT/nF)(1/I_a^0)$ . This is the case for processes with large exchange current densities, and consequently *direct* measurement of rectification current is of limited usefulness for fast reactions.

The rectification voltage, however, can be determined as was shown by Barker<sup>4</sup> by the following method which finds

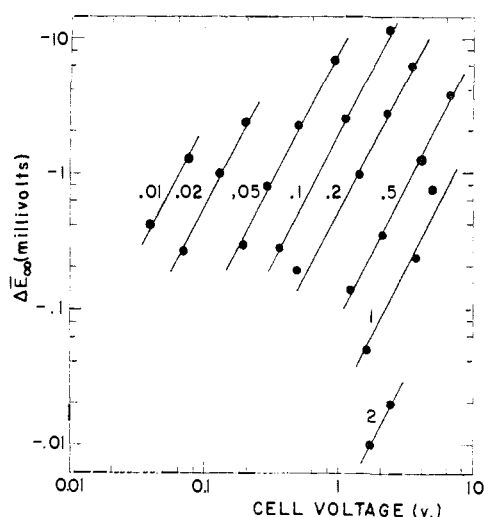


Fig. 6.—Variations of  $\Delta\bar{E}_\infty$  with cell voltage (log-log plot) for 0.7 mM Ti(IV) plus 18.8 mM Ti(III) in 0.88 M  $\text{H}_2\text{SO}_4$  and 0.5 M tartaric acid at different frequencies (in megacycles per sec.). Note that all curves have a slope of 2.

its justification in eq. 21: the rectification current is compared at a sufficiently short time  $t$  with the current (at the same time  $t$ ) which results from the application of a voltage-step to the cell in the absence of alternating current; the voltage-step is equal to the rectification voltage when the two currents are equal at time  $t$ .

#### Rectification Voltage in the Absence of Coupled Chemical Reaction.

**Influence of Applied Voltage.**—Values of  $r_s$  and  $y_s$  derived for the faradaic impedance will now be introduced in eq. 10 and 11. According to Warburg,<sup>20</sup> Randles<sup>21</sup> and Ershler<sup>22</sup> one has ( $i \equiv \text{O or R}$ )

$$r_i = y_i = \frac{RT}{2^{1/2} \omega^{1/2} F^2 C_i^0 D_i^{1/2} \omega^{1/2}} \quad (22)$$

where  $D_i$  is the diffusion coefficient of species  $i$ . Further,  $y_i = 1/\omega c_s$ ,  $c_s$  being the capacity of the series equivalent circuit. Combination of eq. 9 to 11 and 22 then yield

$$\Delta\bar{E}_\infty = \frac{nF}{RT} V_A \left\{ \frac{2\alpha - 1}{4} - \frac{1}{2} \left[ \alpha - \frac{C_O^0 D_O^{1/2}}{C_O^0 D_O^{1/2} + C_R^0 D_R^{1/2}} \right] \frac{1 + \text{ctn } \theta_a}{1 + \text{ctn}^2 \theta_a} \right\} \quad (23)$$

where  $\theta_a$  is the apparent phase shift (no double layer correction) between current and voltage, *i.e.*

$$\text{ctn } \theta_a = \omega r_s c_s \quad (24)$$

It follows that  $\Delta\bar{E}_\infty = 0$  when  $C_O^0 D_O^{1/2} = C_R^0 D_R^{1/2}$  and  $\alpha = 0.5$ , as one would expect. One also infers from eq. 23 that  $\Delta\bar{E}_\infty$  is proportional to  $V_A^2$ . If the cell resistance  $r$  is such that  $r \gg Z$  and  $r \gg 1/\omega c_1$ ,  $\Delta\bar{E}_\infty$  is practically proportional to the square of the cell voltage (Fig. 6 and Table I<sup>23</sup>; note that  $\Delta\bar{E}_\infty$  for a given  $V_A$  is virtually frequency-independent in Table I). It is worth noting that al-

(20) E. Warburg, *Ann. Physik*, **67**, 493 (1899); **6**, 125 (1901).

(21) J. E. B. Randles, *Discussions Faraday Soc.*, **1**, 11 (1947).

(22) (a) B. V. Ershler, *ibid.*, **1**, 269 (1947). (b) B. V. Ershler, *Zhur. fiz. Khim.*, **22**, 683 (1948). (c) K. Rozental and B. V. Ershler, *ibid.*, **22**, 1344 (1948).

(23) It was assumed in the calculation of  $V_A$  that  $1/\omega c_1 \ll Z$ ,  $Z$  being the faradaic impedance. In this instance,  $c_1 = 27.0$  microfarads.  $\text{cm}^{-1}$  as measured with a bridge at 250 cycles per sec.

though theory was developed for values of  $V_A$  not exceeding a few millivolts,  $\Delta\bar{E}_\infty$  is proportional to  $V_A^2$  for values of  $V_A$  exceeding even 50 mV.

TABLE I  
VARIATIONS OF  $\Delta\bar{E}_\infty$  WITH  $V_A$  FOR 0.7 mM Ti(IV) PLUS 18.8 mM Ti(III) IN 0.88 M  $\text{H}_2\text{SO}_4$  AND 0.5 M TARTARIC ACID AT DIFFERENT FREQUENCIES

$f$ , Mc./sec.	$V_A$ , mV.	$-\Delta\bar{E}_\infty$ , mV.	$-\Delta\bar{E}_\infty /$ $V_A^2$ , volt <sup>-1</sup>	$-\Delta\bar{E}_\infty /$ $V_A^2$ , (average) volt <sup>-1</sup>
0.01	15	0.42	1.93	1.79
	28	1.3	1.65	
0.02	13	0.27	1.63	1.72
	24	1.0	1.75	
	37	2.4	1.78	
0.05	14	0.30	1.52	1.67
	22	0.80	1.74	
	36	2.3	1.83	
	67	7.0	1.57	
0.1	13	0.28	1.57	1.60
	40	2.6	1.58	
	85	12	1.66	
0.2	8.8	0.20	2.57	1.86
	26	1.0	1.51	
	40	2.8	1.71	
	63	6.4	1.63	
0.5	8.9	0.14	1.82	1.59
	16	0.36	1.50	
	30	1.3	1.49	
	48	4.0	1.73	
1	5.9	0.05	1.43	1.77
	13	.24	1.35	
	18	.8	2.54	

**Influence of Frequency.**—The effect of frequency on  $\Delta\bar{E}_\infty$  is readily deduced from eq. 23. This matter which was only briefly examined by Barker<sup>4</sup> on the basis of his value of  $\Delta\bar{E}_\infty$  (equivalent to eq. 23) will be considered here. Two terms in eq. 23 must be considered, namely  $V_A$  and  $\text{ctn } \theta_a$ . Variations of  $(1 + \text{ctn } \theta_a)/(1 + \text{ctn}^2 \theta_a)$  with  $\theta_a$  are shown in Fig. 7. The voltage  $V_A$  depends on the double layer differential capacity  $c_1$  and the faradaic impedance  $Z$  and can easily be calculated. Two extreme cases are of interest, namely  $1/\omega c_1 \gg Z$  and  $1/\omega c_1 \ll Z$ , which correspond for a constant cell current to A.C. control and A.V. control, respectively. Two limiting cases will be considered: diffusion control of the faradaic impedance for  $\omega \rightarrow 0$  and control by kinetics of charge transfer for  $\omega \rightarrow \infty$ . One has  $\text{ctn } \theta_a \rightarrow 1$  for diffusion control and

$$\left( \frac{\Delta\bar{E}_\infty}{V_A^2} \right)_{\omega \rightarrow 0} = \frac{nF}{4RT} \frac{C_O^0 D_O^{1/2} - C_R^0 D_R^{1/2}}{C_O^0 D_O^{1/2} + C_R^0 D_R^{1/2}} \quad (25)$$

Since  $V_A \approx I_A/\omega c_1$  for  $1/\omega c_1 \ll Z$ ,  $I_a$  being the amplitude of the alternating current density,  $\Delta\bar{E}_\infty/I_A^2$  is proportional to  $1/\omega^2$  for diffusion-controlled processes. Conversely,  $V_A \approx I_A Z$  for  $1/\omega c_1 \gg Z$  with  $Z$  proportional to  $1/\omega^{1/2}$  for a diffusion-controlled process, and  $\Delta\bar{E}_\infty/I_A^2$  is proportional to  $1/\omega$ .

If  $\omega \rightarrow \infty$ , one has  $V_A \rightarrow 0$  for any finite  $I_A$ , and consequently  $\Delta\bar{E}_\infty \rightarrow 0$ . Further

$$\left( \frac{\Delta\bar{E}_\infty}{V_A^2} \right)_{\omega \rightarrow \infty} = \frac{nF}{4RT} (2\alpha - 1) \quad (26)$$

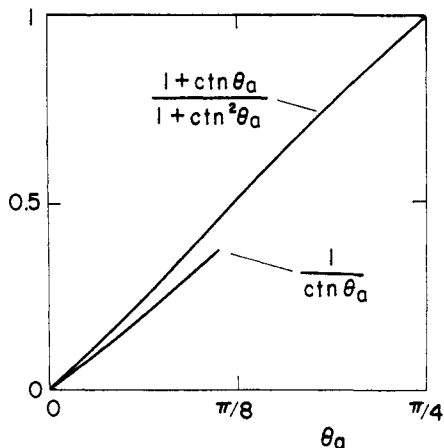


Fig. 7.—Variations of  $(1 + \text{ctn } \theta_a)/(1 + \text{ctn}^2 \theta_a)$  with  $\theta_a$ .

At sufficiently high frequencies,  $\Delta \bar{E}_\infty/V_A^2$  varies linearly with  $1/\omega^{1/2}$ . Thus, one has  $(1 + \text{ctn } \theta_a)/(1 + \text{ctn}^2 \theta_a) \approx 1/\text{ctn } \theta_a$  for  $\text{ctn } \theta_a \gg 1$ , and there follows from eq. 10, 11 and 22

$$\frac{1}{\text{ctn } \theta_a} = \frac{I_a^0}{2^{1/2} n F} \left( \frac{1}{C_O^0 D_O^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \frac{1}{\omega^{1/2}} \quad (27)$$

provided that  $\omega^{1/2} > 10^4 k_a^0 / (k_a^0)$ , apparent standard rate constant of eq. 2,  $D_O = D_R = 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>,  $C_O^0 = C_R^0$ . Under these conditions,  $\Delta \bar{E}_\infty/V_A^2$  varies linearly with  $1/\omega^{1/2}$ . The transfer coefficient  $\alpha$  is obtained from the intercept at  $1/\omega^{1/2} = 0$  and  $I_a^0$  is then calculated from the slope of this plot. As a verification,  $\alpha$  can also be determined from the variations of  $I_a^0$  with reactant concentration.<sup>10</sup>

Possible dispersion of the differential capacity of the double layer with frequency should not be overlooked in the calculation of  $V_A$  at different frequencies.

Experimental data in Fig. 8 for the discharge of Hg(I) on mercury confirm these conclusions for diffusion-controlled processes. At low Hg(I) concentrations, the condition  $1/\omega c_1 \ll Z$  is approached and  $\Delta \bar{E}_\infty/I_A^2$  is proportional to  $1/\omega^2$  as it should. Conversely, at high Hg(I) concentrations, the condition  $1/\omega c_1 \gg Z$  is approached, and  $\Delta \bar{E}_\infty/I_A^2$  should vary with  $1/\omega$ , as is indeed the case for the lower frequencies in Fig. 8. Further,  $\Delta \bar{E}_\infty/I_A^2$  for pure diffusion control should be independent of the Hg(I) concentration according to eq. 25. This is indeed the case for the three lowest concentrations in Fig. 8. Extrapolation of  $\Delta \bar{E}_\infty/V_A^2$  to  $\omega = 0$  for the three lowest concentrations gave the limiting value  $\Delta \bar{E}_\infty/V_A^2 = 20 \pm 5$  volt<sup>-1</sup> for an assumed differential capacity  $c_1$  of 160 microfarad. cm.<sup>-2</sup>. This is the limiting value  $\Delta \bar{E}_\infty/V_A^2 = nF/4RT$  for  $\omega = 0$  and  $n = 2$  for a diffusion-controlled process. No accurate verification was possible since  $c_1$  could not be measured in this case. As order of magnitude one can set  $c_1 \approx 100$  farad. cm.<sup>-2</sup> from double pulse galvanostatic measurements.<sup>18</sup>

The frequency dependence for processes nearly controlled by charge transfer was not studied here because the upper frequency of 2 megacycles per sec. of the available instrument was not sufficiently high for accurate study of Hg(I) discharge. This matter will be taken up when an instrument for higher frequencies now under construction is available.

**Variations of  $\Delta \bar{E}_\infty/V_A^2$  with the Ratio  $C_O^0/C_R^0$ .**—Barker<sup>4</sup> examined the variations of a quantity which is proportional to  $\Delta \bar{E}_\infty/V_A^2$  with the ratio  $C_O^0/C_R^0$  (i.e. with the equilibrium potential). Two limiting cases for which eq. 25 and 26 apply, respectively, will be considered:  $\omega \rightarrow 0$  and  $\omega \rightarrow \infty$ .

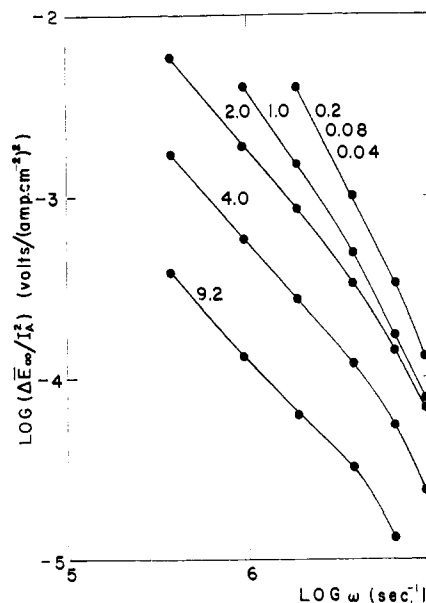


Fig. 8.—Plot of  $\log (\Delta \bar{E}_\infty/I_A^2)$  against  $\log \omega$  for the discharge of Hg(I) at different concentrations (mM per liter) on mercury in 1.14 M HClO<sub>4</sub>.  $\Delta \bar{E}_\infty$  was negative for all concentrations.

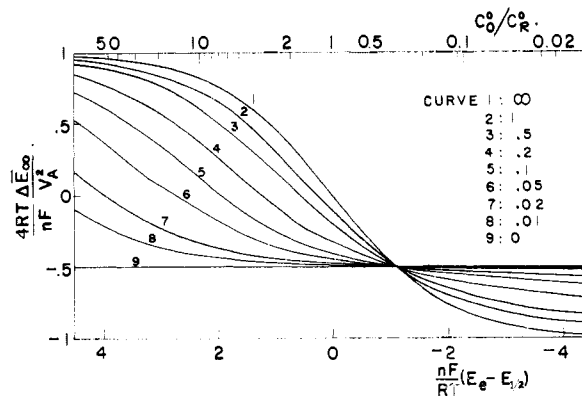


Fig. 9.—Plot of  $(4RT/nF)(\Delta \bar{E}_\infty/V_A^2)$  against  $(nF/RT)(E_0 - E_{1/2})$  for different values of  $k_a^0/(2\omega D)^{1/2}$ ,  $D$  being the common value of  $D_O$  and  $D_R$ , and for  $\alpha = 0.25$ .

$\Delta \bar{E}_\infty/V_A^2$  for  $\omega \rightarrow 0$  varies with

$$(C_O^0 D_O^{1/2} - C_R^0 D_R^{1/2}) / (C_O^0 D_O^{1/2} + C_R^0 D_R^{1/2})$$

This quantity approaches  $\pm 1$  for  $E_e \rightarrow \pm \infty$  and is equal to zero at the polarographic half-wave potential. Hence  $\Delta \bar{E}_\infty/V_A^2 = \pm nF/4RT$  for  $E_e \rightarrow \pm \infty$  and  $\omega \rightarrow 0$ . Equation 25 applies for  $\omega \rightarrow \infty$ , and one has  $\Delta \bar{E}_\infty/V_A^2 \geq 0$  for  $\alpha \geq 0.5$ . An intermediate curve having the lines  $\Delta \bar{E}_\infty/V_A^2 = \pm nF/4RT$  as asymptotes is obtained for mixed control of the faradaic impedance by mass and charge transfer (Fig. 9). All curves intersect at the point having the ordinate given by eq. 26 and the abscissa obeying the equation

$$\tanh \left[ \frac{1}{2} \frac{nF}{RT} (E_e - E_{1/2}) \right] = (2\alpha - 1) \quad (28)$$

The parameter  $\alpha$  thus can be computed in two ways from the coordinates of the intersection point.

Experimental curves for the Ti(IV)-Ti(III) couple in Fig. 10 have the same general shape as



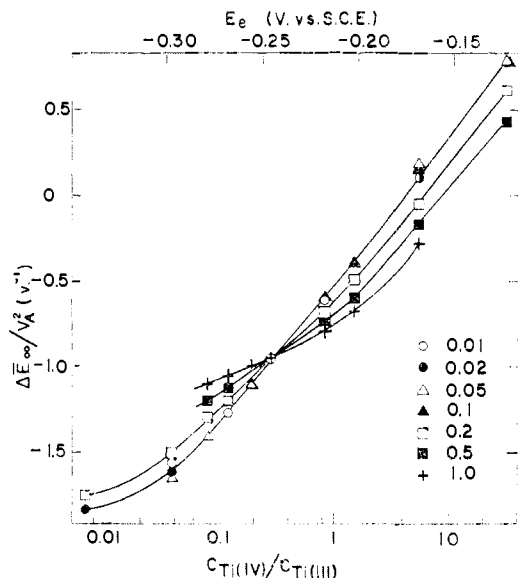


Fig. 10.—Plot of  $\Delta E_{\infty}/V_A^2$  against  $C_{\text{Ti(IV)}}/C_{\text{Ti(III)}}$  for  $\text{Ti(IV)} - \text{Ti(III)}$  in  $0.88 M \text{H}_2\text{SO}_4$  and  $0.5 M$  tartaric acid for different frequencies (in megacycles per sec.).  $C_{\text{Ti(IV)}}^0 + C_{\text{Ti(III)}}^0 = 19.5 \text{ mM}$  per liter. Experimental points at the common intersection point nearly coincide for all frequencies and are not indicated for the sake of clarity. The same remark also holds for some of the other measurements.

the theoretical curves of Fig. 9. The experimental curves also exhibit a single intersection point, from whose coordinates one calculates  $\alpha = 0.25$  (abscissa) and  $\alpha = 0.46$ . No conclusive interpretation can be given for this discrepancy, but there are at least two possible explanations: the influence of adsorbed tartaric acid which complicates the interpretation and the possibility of a chemical reaction preceding or following the charge transfer reaction (see below).

**Correction for the Double Layer Structure in the Absence of Specific Adsorption and beyond the Frumkin Theory.**—Values of the  $r$ 's and  $y$ 's which were introduced in eq. 9 and which led to eq. 23 for  $\Delta E_{\infty}$  were taken from the classical theory of the faradaic impedance, *i.e.*, the structure of the double layer was not considered in the boundary value problem in the derivation of  $\Delta E_{\infty}$ . The approximation is quite crude since the attenuation factor (equivalent to the diffusion layer thickness) for the concentration waves,  $(2D/\omega)^{1/2}$ , is not extremely large in comparison with the diffuse double layer thickness, *e.g.*,  $(2D/\omega)^{1/2} \approx 3 \times 10^{-6} \text{ cm.}$  for  $D = 10^{-6} \text{ cm.}^2 \text{ sec.}^{-1}$  and  $f = 1$  megacycle per sec. This effect of the double layer, which is beyond the Frumkin correction for the double layer structure,<sup>24</sup> was analyzed in this Laboratory.<sup>25</sup> The correction for  $\Delta E_{\infty}$  was already discussed by Matsuda and Delahay,<sup>6</sup> and their results will be briefly reviewed in the light of the general theory presented here.

Correction is made by introduction in eq. 9 of the values of  $r$ 's and  $y$ 's derived by Matsuda.<sup>25b</sup> Equation 23 is still valid but its right-hand member now includes as a first approximation the additional term

$$-\frac{V_A^2}{2nF} \left[ \frac{\alpha \zeta_0}{\kappa C_O^0 D_O} - \frac{(1-\alpha)\zeta_R}{\kappa C_R^0 D_R} \right] \frac{r_s}{r_s + y_s^2}$$

where  $r_s$  and  $y_s$  are given by eq. 10 and 11,  $1/\kappa$  is the so-

(24) For a recent review see Chapter 1 by R. Parsons in "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and C. W. Tobias, editors, Interscience Publishing Co., New York, N. Y., in course of publication. See also Chapter 2 by A. N. Frumkin

(25) (a) H. Matsuda and P. Delahay, *J. Phys. Chem.*, **64**, 332 (1960). (b) H. Matsuda, *ibid.*, **64**, 339 (1960).

called thickness of the diffuse double layer and  $\zeta_0$  and  $\zeta_R$  are parameters depending on the double layer structure (*cf.* eq. 4 and 21 in ref. 25b). The limit of this additional term should also be included in the value of  $\Delta E_{\infty}$  for  $\alpha \rightarrow \infty$  (see eq. 25). (Note that  $r_s/(r_s + y_s^2) \rightarrow (nF/RT)I_{a0}$  for  $\alpha \rightarrow \infty$ .) Further analysis of this problem in this Laboratory has shown that the above correction holds only when  $\zeta_0$  and  $\zeta_R$  are sufficiently small to satisfy the conditions stated in ref. 25a and 25b.

#### Rectification Voltage for a Charge Transfer Reaction with Preceding Chemical Reaction.

This case, which was discussed by Barker<sup>4c</sup> on the basis of an absolutely equivalent circuit (by the use of transmission lines), is readily analyzed from the general equation 9. The values of  $r$ 's and  $y$ 's derived by Gerischer<sup>26</sup> for the faradaic impedance in this instance must now be used. We only consider the first order or pseudo-first order reaction  $X \rightleftharpoons 0$  preceding charge transfer since equations for higher order reactions can be linearized for a small departure from equilibrium. The following term

$$(r_{rp})_0 = \frac{RT}{(nF)^2} \frac{1}{2^{1/2}} \frac{1}{C_O^0 D^{1/2}} \frac{1}{K} \left\{ \frac{(\omega^2 + l^2)^{1/2} + l}{\omega^2 + l^2} \right\}^{1/2} \quad (29)$$

must be added to  $r_s$  and  $r_0$  and the term

$$(y_{rp})_0 = \frac{RT}{(nF)^2} \frac{1}{2^{1/2}} \frac{1}{C_O^0 D^{1/2}} \frac{1}{K} \left\{ \frac{(\omega^2 + l^2)^{1/2} - l}{\omega^2 + l^2} \right\}^{1/2} \quad (30)$$

must be added to  $y_s$  and  $y_0$ . The values of  $r_R$  and  $y_R$  remain unchanged (*cf.* eq. 22) since R is not involved in a chemical reaction. Notations in eq. 29 and 30 are:  $D$  the common value of the diffusion coefficients of X and O supposed to be equal,  $K = C_O^0/C_X^0$  the equilibrium constant,  $C^0 = C_O^0 + C_X^0$ , and  $l = k_t + k_b$ ,  $k_t$  and  $k_b$  being the rate constants for  $X \rightleftharpoons 0$ .

The reaction polarization resistance  $(r_{rp})_0$  of eq. 29 is frequency independent in the limiting case corresponding to  $\omega \ll l$ , and  $(y_{rp})_0$  is then equal to zero. Conversely,  $(r_{rp})_0$  and  $(y_{rp})_0$  are equal and are proportional to  $1/\omega^{1/2}$  when  $\omega \gg l$ . Further,  $(r_{rp})_0$  and  $(y_{rp})_0$  approach zero for  $1/\omega^{1/2} \rightarrow 0$ . If the general eq. 9 or its particular form in eq. 23 is applied without consideration of a chemical reaction, the measured transfer coefficient, as deduced from eq. 26 by extrapolation with  $1/\omega^{1/2}$ , may be in error. If the charge transfer resistance  $r_{ct}$  is such that  $r_{ct} \gg (r_{rp})_0$  at the highest frequencies being used, the error on  $\alpha$  is negligible. Conversely, when  $r_{ct} \ll (r_{rp})_0$  at the highest frequencies being investigated, one deduces from eq. 9 that  $\Delta E_{\infty} \rightarrow (-1/4)(nF/RT)V_A^2$  for  $\omega \rightarrow \infty$ , *i.e.*,  $\alpha$  apparently approaches zero for the upper limit of  $\omega$ 's being used when the effect of the chemical reaction is overlooked. This conclusion is in agreement with Barker's observation<sup>4c</sup> that abnormally low apparent transfer coefficients are obtained for discharge of certain metal ions.

This discussion can readily be extended to charge transfer processes preceded by a heterogeneous chemical reaction since there is a formal analogy between the treatment of this case and the above analysis. This extension is valid provided that steady state is reached for the heterogeneous chemical reaction.

#### Limitations Resulting from the Cell Resistance

Limitations are imposed by two conditions for the time  $t$  at which  $\Delta E_{\infty}$  is measured:  $t$  must be long enough to allow

(26) H. Gerischer, *Z. physik. Chem.*, **198**, 286 (1951).

$\Delta E_{\infty}$  to be reached but  $t$  must be short enough to prevent undesirable local heating of the solution. Corrections could possibly be worked out when these two conditions are not satisfied, and the limit of measurable  $I_A$ 's could be increased.

Attainment of  $\Delta E_{\infty}$  does not raise any problem for fast reactions since the charging of the double layer is then very rapid under proper conditions. Further, the alternating cell current must practically attain its steady-state value. Steady state is reached within 1% for  $t > 5\tau$ ,  $\tau$  being the total resistance of the circuit connected to the alternating current generator and  $c$ , for control at  $I = 0$ , the capacity equivalent to the series combination of the double layer differential capacity and the capacity in series with the cell (see the end of the Qualitative Discussion). The latter capacity which generally should not exceed 0.01 microfarad for a cell with a dropping mercury electrode is determinative, and the condition for steady state attainment for usual values of  $\tau$  ( $\tau = 100$  ohms) is  $t > 5$  microseconds. This is not a stringent condition.

The upper limit of  $t$  is generally determined by the maximum allowable rise in temperature of the electrolyte near the electrode. The change in equilibrium potential due to temperature rise must indeed be small in comparison with  $\Delta E_{\infty}$ . Since  $|\Delta E_{\infty}| < (nF/4RT)V_A^2$  and  $V_A \leq 0.005$  volt (this limit might possibly be raised), one has  $|\Delta E_{\infty}| \approx 100n$  to  $200n$  microvolts. Further  $|dE_e/dt| \leq 1$  millivolt deg.<sup>-1</sup> in general, and consequently one should have  $\Delta T < 0.001$  to  $0.01$  degree. A conservative estimate of the maximum allowable time for measurement is readily obtained on the assumption that there is no heat transfer in solution and between solution and the electrode. One has for an electrode with uniform current density  $dT/dt = 0.24(I_A^2/2)(1/\kappa_s \delta_0 C_h)$  at the electrode surface,  $\kappa_s$  being the specific conductance of the electrolyte,  $C_h$  its specific heat and  $\delta_0$  its density. For instance, for a 1 molar aqueous solution of a strong acid one has at room temperature  $dT/dt = 0.3 I_A^2$  deg. sec.<sup>-1</sup> or for  $I_A = 1$  amp. cm.<sup>2</sup> (an order of magnitude for  $f = 1$  megacycle per sec.),  $dT/dt = 0.3$  deg. sec.<sup>-1</sup>. Since one should have  $\Delta T < 0.001$  to  $0.01$  degree,  $\Delta E_{\infty}$  must be measured within 3 to 30 milliseconds in this particular case. Such measurements are made by pulse techniques. A correction could of course be made for the temperature change, but it would require the solution of the boundary value problem for heat transfer.

The large ohmic drop for the alternating current is eliminated in the measurement of  $\Delta E_{\infty}$  by means of a low pass filter. Requirements for this filter become more stringent as the resistance increases as one can readily show. Thus,  $\Delta E_{\infty}$  is proportional to  $V_A^2$ , i.e., to the square of the alternating voltage  $V$  applied to the cell provided that  $\tau \gg Z$  and  $\tau \gg 1/\omega c_1$ ,  $\tau$  being the cell resistance and  $c_1$  the differential capacity of the double layer. The output alternating voltage of a one-section inductance-capacity filter  $V_{out}$  in its cut off range is proportional to the input voltage and inversely proportional to  $\omega^m$  where usually  $m = 2$ . Hence  $\Delta E/V_{out}$  is proportional to  $V$  and inversely proportional to  $\tau^2$ .

### Experimental

**Solutions.**—Solutions were prepared from analytical grade reagents (except for Ti(III)) and bidistilled water (over  $\text{KMnO}_4$ ). The stock solution of Hg(I) in perchloric acid was standardized by electrogravimetry after reduction of traces of Hg(II) by mercury. Traces of adsorbable organic impurities were removed by treatment with purified charcoal according to Barker.<sup>46</sup> Charcoal was purified by a two-week extraction with HCl in a Soxhlet extractor (without cartridge) followed by a one-week extraction with frequently renewed distilled water.

The Ti(IV)-Ti(III) solutions were prepared from a 20%  $\text{TiCl}_3$  aqueous solution (Matheson Co., Inc.). This solution contained an appreciable amount of zinc as was found by polarography but this impurity did not interfere. The titanium solution was analyzed as follows: aliquot sample was oxidized by  $\text{H}_2\text{O}_2$ ; chloride was removed by heating with  $\text{H}_2\text{SO}_4$  to fuming; Ti(IV) was finally reduced to Ti(III) and titrated with  $\text{KMnO}_4$  in a nitrogen atmosphere. The Ti(IV)/Ti(III) ratio was changed by complete reduction with zinc amalgam followed by partial oxidation by bubbling of oxygen. Finer control was achieved by the mixing of completely oxidized and reduced solutions. The Ti(IV)/Ti(III) ratio was determined *in situ* in the cell by polarography from the cathodic and anodic diffusion

currents. The ratio obtained in this fashion agreed well with the ratios calculated from equilibrium potentials.

**Cell.**—A polarographic H-cell was used with dropping mercury electrode and mercury pool in the same arm. The other arm of the cell was filled with a 1 M solution of ammonium nitrate (for the  $\text{Hg}_2^{++}$  study) or 0.88 M sulfuric acid (for the Ti study) and connected with a saturated KCl bridge to a saturated calomel electrode. Precipitation of potassium perchlorate or potassium hydrogen tartrate was thus avoided. The cell was immersed in a water-bath, the water of which was made conducting by salt addition. This provided adequate shielding for the cell. The dropping mercury electrode was fitted with a magnetic hammer for synchronization of drop fall with oscillographic recordings.

**Current-Potential Curves.**—A Sargent polarograph model XXI was used according to conventional practice. Recordings were made with the saturated calomel electrode (and not the Hg-pool) as reference electrode.

**Double Layer Differential Capacities.**—Measurements were made according to Grahame.<sup>27</sup>

**Rectification Voltage.**—Rectification voltages were measured during a short single pulse for each consecutive drop at the dropping mercury electrode. Oscilloscopic display of the rectification voltage was synchronized with the fall of the mercury drop by means of magnetic hammer and a timing device. The output of a Hewlett-Packard oscillator model 200 CD (up to 0.6 Mc) or General Radio oscillator model 1211-B (above 0.5 Mc) was 100% modulated by a Tektronix preamplifier 53-54 C used as gate. The modulating pulse obtained from a Tektronix pulse generator model 163 was properly synchronized with the drop fall. The Tektronix preamplifier 53-54 C was inserted in a Tektronix oscilloscope model 536, and a 15 volt modulated signal was thus obtained. This signal was further amplified with a Tektronix amplifier model 112 to approximately a 100 volt signal. The latter was applied to a conventional power amplifier using two 6AS7G tubes in parallel. The maximum output was 5 volts across 50 ohms at frequencies up to 2 megacycles per sec. Rectification voltages were measured with a Tektronix oscilloscope model 531 equipped with a preamplifier model 53-54 E. The maximum sensitivity was 50 microvolts per cm. The low pass filter between the cell and the input of the preamplifier was composed of General Radio adjustable decade capacitor and inductance boxes, model 1419-K and 1490-C, respectively. The settings on these boxes were adjusted according to the frequency. In general, values of  $\Delta E_{\infty}$  was read on the screen of the oscilloscope. A number of photographs were also made. The alternating voltage across the cell was displayed during the single pulse measurement on a Tektronix oscilloscope model 535 with preamplifier model 53-54 G.

**Experimental Conditions.**—For the  $\text{Hg}_2^{++}$  study: cell resistance, 52 ohms (mostly due to the mercury column of d.m.e.);  $m$  for d.m.e., 1.01 mg. sec.<sup>-1</sup>;  $\tau$  without synchronization,  $\approx 6$  sec.;  $\tau$  synchronized, 5.02 sec.;  $t$  at the beginning of r.f. pulse, 3.7 or 1.3 sec. (to provide areas of  $2.06 \times 10^{-2}$  and  $1.03 \times 10^{-2}$  cm.<sup>2</sup> in the ratio 2:1).

For the Ti(IV)-Ti(III) system: cell resistance, 56 ohms;  $m$  for d.m.e., 1.65 mg. sec.<sup>-1</sup>;  $\tau$  without synchronization  $\approx 6$  sec.;  $\tau$  synchronized, 5.02 sec.;  $t$  at the beginning of r.f. pulse, 3.7 sec.

The temperature was  $30 \pm 0.1^\circ$  in all experiments.

### Conclusion

A general theory of faradaic rectification was developed, and it was shown that both the mean and the alternating components of potential and/or current must be controlled. Transients due to charging of the double layer and to rectification by the double layer are quite essential in the interpretation of rectification voltage measurements.

The difficulties associated with the double layer capacity and ohmic drop in other relaxation methods are largely eliminated in the application of faradaic rectification to very fast reactions. The

(27) D. C. Grahame, *THIS JOURNAL*, **68**, 301 (1946); **71**, 2975 (1949).

method has two unique features in that (a) conditions in which the cell alternating current is primarily controlled by the double layer capacity do not prevent measurement of  $I_a^0$  and  $\alpha$  but in fact are desirable (A.V. control), and (b) frequency discrimination by means of a low pass filter in the measurement of  $\Delta\bar{E}_\infty$  eliminates the difficulty resulting from a large ohmic drop and allows the determination of  $I_a^0$  and  $\alpha$  even when the cell resistance is very much larger than the charge transfer resistance.

An upper limit of the  $k_a^0$ 's which could be determined can be set only after further evaluation but it appears that values of  $k_a^0$  up to 10 to 100 cm. sec.<sup>-1</sup> could be measured. The upper limit is based on the fairly reasonable assumption that frequencies up to 100 megacycles per sec. can be used (perhaps with some difficulties). The question arises at very high frequencies whether formulas derived from Fick's equation for diffusion still apply since motion can no longer be regarded as completely randomized. Such considerations, however, need not be introduced below 100 megacycles per sec. (or perhaps even higher frequencies) since the average path of a diffusing particle ( $D = 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>) for  $t = 10^{-8}$  sec. is still quite large in comparison with molecular dimensions.

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### Appendix

**Derivation of Equation 9.**—As noted above, eq. 9 is deduced from eq. 5 in which  $\delta_0^2 I$  is derived from eq. 4. Further, the terms in  $\partial^2 I / \partial C_0^2$ ,  $\partial^2 I / C_R^2$  and  $\partial^2 I / \partial C_0 \partial C_R$  in eq. 4 vanish if one assumes, as will be the case here, that the  $I$ - $E$  characteristic is linear in the concentrations of O and R (cf. eq. 1). The problem thus is to express  $\delta C_0$  and  $\delta_1 C_R$  of eq. 4 in terms of the resistive and capacitive elements of the series equivalent circuit for the faradaic impedance.

Quite generally one has with the conventions of sign or eq. 1

$$\delta_1 I = - \frac{\delta_1 E}{r_s - j y_s} \quad (31)$$

where  $r_4$  and  $y_5$  are the resistive and capacitive elements of the series equivalent circuit for the faradaic impedance (cf. eq. 10 and 11). Further, if one assumes that the kinetic parameters for the supply and/or removal of O and R (diffusion, homogeneous or heterogeneous chemical reaction, etc.) are independent of potential, one has for species  $i$  ( $\pm$ O or R)

$$\delta_1 C_i = \mp [(h_r)_i - j(h_y)_i] \delta_1 I \quad (32)$$

where the  $\mp$  sign holds for O and R, respectively, and  $h_r$  and  $h_y$  are constants which depend only on the processes for supply and/or removal of O and R between the bulk of solution and the electrode. By introduction of  $\delta_1 C_i$  from eq. 32 into

$$\delta_1 I = \frac{\partial I}{\partial E} \delta_1 E + \frac{\partial I}{\partial C_0} \delta_1 C_0 + \frac{\partial I}{\partial C_R} \delta_1 C_R \quad (33)$$

one obtains after re-arrangement of terms

$$\delta_1 I = - \frac{\delta_1 E}{\frac{\partial I}{\partial E} + \frac{\partial I}{\partial C_0} [(h_r)_R - \frac{\partial C_0}{\partial E} (h_r)_O - j \left[ \frac{\partial I}{\partial C_R} (h_y)_R - \frac{\partial C_0}{\partial E} (h_y)_O \right]} \quad (34)$$

or

$$\delta_1 I = - \frac{\delta_1 E}{r_{ct} + r_R + r_O - j(y_R + y_O)} \quad (35)$$

where  $r_{ct}$ ,  $r_O$ ,  $r_R$ ,  $y_R$ ,  $y_O$  are defined in conjunction with eq. 10 and 11. The values of the  $r$ 's and  $y$ 's are readily written by comparison of eq. 34 and 35. By introducing in eq. 32 the  $r$ 's and  $y$ 's thus obtained one derives for species  $i$  ( $i \equiv$  O or R)

$$\delta_1 C_i = [(\partial I / \partial E) / (\partial I / \partial C_i)] (r_i - j y_i) \delta_1 I \quad (36)$$

or after combination with eq. 31.

$$\delta_1 C_i = - [(\partial I / \partial E) / (\partial I / \partial C_i)] \frac{r_i - j y_i}{r_s - j y_s} \delta_1 E \quad (37)$$

A general equation for  $\delta_0^2 I$  of eq. 5 can thus be written from eq. 4 and 37. Equation 9 was derived by substitution of these values corresponding to eq. 1 for the partial derivatives at  $E_c$ :  $\partial I / \partial E = -I_a^0 (nF/RT)$ ,  $\partial I / \partial C_0 = I_a^0 / C_0^0$ ,  $\partial I / \partial C_R = -I_a^0 / C_R^0$ ,  $\partial^2 I / \partial E^2 = I_a^0 [\alpha^2 - (1 - \alpha)^2]$ ,  $\partial^2 I / \partial E \partial C_0 = -(I_a^0 / C_0^0) / (\alpha nF/RT)$ ,  $\partial^2 I / \partial E \partial C_R = -(I_a^0 / C_R^0) [(1 - \alpha) nF/RT]$ ,  $-(\partial I / \partial E) / (\partial I / \partial C_0) = (nF/RT) C_0^0$  and  $-(\partial I / \partial E) / (\partial I / \partial C_R) = -(nF/RT) C_R^0$ .