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Faradaic Rectification and Electrode Processes.

Carl Herrmann Weis  
*Louisiana State University and Agricultural & Mechanical College*

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AND

ELECTRODE PROCESSES

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in

The Department of Chemistry

by

Carl Hermann Weis
Industrial Chemist, University of Rio Grande do Sul, (Brazil), 1952
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August, 1960
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>ABSTRACT</th>
<th>vii</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAPTERS</td>
<td></td>
</tr>
<tr>
<td>I.  INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1) Nature and Purpose of Faradaic Rectification</td>
<td>1</td>
</tr>
<tr>
<td>2) Previous Work.</td>
<td>3</td>
</tr>
<tr>
<td>3) Qualitative Discussion of Types of Control</td>
<td>5</td>
</tr>
<tr>
<td>4) Purpose of This Work</td>
<td>13</td>
</tr>
<tr>
<td>II. EXPERIMENTAL METHODS</td>
<td>15</td>
</tr>
<tr>
<td>1) Solutions.</td>
<td>15</td>
</tr>
<tr>
<td>2) Cell</td>
<td>16</td>
</tr>
<tr>
<td>3) Instrumentation</td>
<td>17</td>
</tr>
<tr>
<td>4) Details on Measurements</td>
<td>27</td>
</tr>
<tr>
<td>5) Summary of Experimental Conditions</td>
<td>29</td>
</tr>
<tr>
<td>III. COMPARISON OF THEORY AND EXPERIMENTAL RESULTS</td>
<td>31</td>
</tr>
<tr>
<td>1) Rectification Voltage and Mean Rectification Current Density</td>
<td>31</td>
</tr>
<tr>
<td>2) Influence of the Double Layer Capacity for Control of ( I ) at Zero</td>
<td>35</td>
</tr>
<tr>
<td>3) Rectification Voltage in the Absence of Coupled Chemical Reaction</td>
<td>43</td>
</tr>
<tr>
<td>4) Limitations Resulting from the Cell Resistance</td>
<td>55</td>
</tr>
<tr>
<td>5) Generation of One Reactant in Situ</td>
<td>58</td>
</tr>
<tr>
<td>IV. CONCLUSIONS</td>
<td>60</td>
</tr>
<tr>
<td>1) Potentialities of the Method</td>
<td>60</td>
</tr>
<tr>
<td>2) Suggestions for Further Work</td>
<td>61</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLES</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Variation of $\Delta E_\infty$ with $V_A$ for 0.7 mM Ti(IV) plus 18.8 mM Ti(III) in 0.88 M sulfuric acid and 0.50 M tartaric acid at different frequencies.</td>
<td>46</td>
</tr>
<tr>
<td>II Differential capacity of the supporting electrolyte (0.88 M sulfuric acid and 0.50 M tartaric acid) for the Ti(IV)/Ti(III) system at 250 cycles per sec.</td>
<td>47</td>
</tr>
<tr>
<td>III Data for $\Delta E_\infty$ for the discharge of 1.0 mM Hg$^{2+}$ in 1.14 M perchloric acid for two electrode areas.</td>
<td>48</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>41</td>
</tr>
<tr>
<td>8</td>
<td>42</td>
</tr>
</tbody>
</table>
9 Variations of $\Delta E_{\infty}$ with the cell R.F. voltage (log-log plot) for 0.7 mM Ti(IV) plus 18.8 mM Ti(III) in 0.88 M sulfuric acid and 0.50 M tartaric acid at different frequencies (in megacycles per sec.).

10 Plot of $\log (\Delta E_{\infty}/I_A^2)$ versus $\log$ for the discharge of Hg$^{2+}$ at different concentrations (mM per liter) in 1.14 M perchloric acid. $\Delta E_{\infty}$ was negative for all concentrations.

11 Plot of $(4RT/nF)(\Delta E_{\infty}/V_A^2)$ against $(nF/RT)(E_e-E_i)$ for different values of $k_a/(2\omega D)$, $D$ being the common value of $D_O$ and $D_R$. $\alpha = 0.25$. Values of $k_a/(2\omega D)$ for curves 1 to 9: $\infty$, 1, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, zero.

12 Plot of $\Delta E_{\infty}/V_A^2$ against $C_{T_5(IV)}/C_{T_5(III)}$ for Ti(IV)-Ti(III) in 0.88 M sulfuric acid and 0.50 M tartaric acid for different frequencies (in megacycles per sec.). $C_{T_5(IV)}+C_{T_5(III)} = 19.5$ mM.

13 Diagram for discussion of filter limitations.
ABSTRACT

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 second. Experimental results for discharge of mercurous ion in perchloric acid on mercury and the Ti(IV) - Ti(III) couple in tartaric acid medium at a dropping mercury electrode are given.

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 ($\bar{I} = 0$) or the mean potential is equal to the equilibrium potential ($\bar{E} = E_e$). 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 derived by Delahay, Senda and Weis for the rectification voltage for control at $\bar{I} = 0$ without assumption about the form of the I-$E$ characteristic is verified experimentally as well as particular forms of this equation in terms of the resistive and capacitive components of the series equivalent circuit for the faradaic impedance.

The time-dependence of the rectification voltage as derived by Delahay, Senda and Weis by consideration of the double layer charging without and with rectification from the double layer is also verified
experimentally. The influence of the applied voltage, frequency and reactant concentrations is discussed and studied experimentally. Limitations imposed by the circuit resistance and the possibility of generation of one reactant in situ are also covered.

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.
CHAPTER I

INTRODUCTION

1) Nature and Purpose of Faradaic Rectification Study

The current—potential relationship for an electrode process is determined by the charge transfer process, the mass transfer processes for reactants and products of reaction, and possibly by homogeneous or heterogeneous chemical reactions coupled with the charge transfer process. The main goals of electrochemical kinetics are (a) to characterize the charge transfer process by kinetic parameters (b) to measure these parameters; and (c) most importantly, to use these parameters in elucidation and correlation of reaction mechanisms. A number of methods have been developed for that purpose among which faradaic rectification is the least applied and least understood. This method is based on the study of the rectification occurring at an electrode-electrolyte boundary when the current and electrode potential are periodic functions of time at rather high frequencies (up to several megacycles per sec.).

In order to discuss the fundamental principles involved and the reason for such a study we shall review briefly some fundamentals of electrode kinetics along the lines of a recent review on the subject.¹

We consider a simple electrode reaction corresponding to the equation

\[ \text{O} + n\text{e} \rightleftharpoons \text{R} \quad (1-1) \]

where both components are soluble in the electrolyte and/or electrode. According to ideas of Butler (1924), Erdey-Gruz and Volmer (1930), the current density-potential relationship for this process is

\[ I = I_a^0 \left\{ \exp \left[ -\frac{\alpha nF}{RT} \eta \right] - \exp \left[ -\frac{(1-\alpha)nF}{RT} \eta \right] \right\} \quad (1-2) \]

where \( I_a^0 \) is the apparent exchange current density, a parameter of the reaction kinetics; \( \alpha \), the transfer coefficient, a second parameter necessary to characterize the reaction kinetics; \( \eta \) equal to \( E - E_e \), is the overvoltage, i.e., the difference between the electrode potential \( E \) at the current density \( I \) and the equilibrium potential \( E_e \) at \( I = 0 \). \( R, T, F \) have their usual physical chemistry meaning. If there is mass transfer polarization, i.e., if there is slow supply of reactants and/or slow removal of products, equation (1-2) becomes

\[ I = I_a^0 \left\{ \frac{C_0^0}{C_0^o} \exp \left[ -\frac{\alpha nF}{RT} \eta \right] - \frac{C_R^0}{C_R^0} \exp \left[ -\frac{(1-\alpha)nF}{RT} \eta \right] \right\} \quad (1-3) \]

where \( C_0^0 \) and \( C_R^0 \) are the concentrations outside the diffusion layer; \( C_0 \) and \( C_R \) are the concentrations at the electrode in the absence of any double layer correction for the concentration profiles. If \( \eta \) is small (\( |\eta| \ll \frac{RT}{\alpha nF} \)) equation (1-3) can be linearized with good approximation. Thus

\[ -\left( \frac{\partial \eta}{\partial I} \right)_{I \to 0} = \frac{RT}{nF} \left[ \frac{1}{C_0^0} \left( \frac{\partial C_0}{\partial I} \right)_{I \to 0} + \frac{1}{C_R^0} \left( \frac{\partial C_R}{\partial I} \right)_{I \to 0} + \frac{1}{I_a^0} \right] \quad (1-4) \]

from equation (1-4) we can see that the current density potential relationship depends on terms due to kinetic parameters (\( 1 / I_a^0 \)) and on mass transport (\( \partial C / \partial I \)). It follows from equation (1-4) that
in order to study inherently fast reactions, i.e., reactions with a
large exchange current density, we have to minimize the mass transfer
terms in equation (1-4). This is achieved by measurements either of
short duration (down to one microsecond) or at high frequencies.

According to equation (1-3) the current density-potential re-
lationship is not linear and is not necessarily symmetrical, i.e.,

\[ I(\gamma) \neq I(-\gamma) \quad (1-5) \]

non-linearity and asymmetry of this current density-potential curve
causes rectification as is well known from the study of \( I - E \) charac-
teristics in electrical circuit theory. Faradaic rectification gives
information on the electrode reaction kinetics through measurement of
rectification effects. High frequencies are chosen to render intrinsic
kinetics effects predominant over mass transport effects.

2) Previous Work

Faradaic rectification was discovered by Doss and Agarwall\(^2\) who
designated it as the "redoxokinetic" effect. The expression "faradaic
rectification" used here was coined by Oldham.\(^3\) Doss and Agarwall\(^4\)
derived the shift of mean potential for a particular control in the

\(^2\) K.S.G. Doss and H. P. Agarwall, "A New Polarization Effect:

\(^3\) K. B. Oldham, "Faradaic Rectification: Theory and Applications
to the \( \text{Hg}_2^2/\text{Hg} \) Electrode," Trans. Faraday Soc. 52, 80 (1957).

\(^4\) K.S.G. Doss and H. P. Agarwall, "The Theory of the Redoxokinetic
Effect and a General Method for the Determination of \( \alpha \) of absolute
special case of reactants and products having equal concentrations and
diffusion coefficients. These authors also pointed out the applications
to kinetics. Barker, Faircloth, and Gardner treated the same problem
without the above restrictive conditions and were the first to fully
realize and demonstrate the potentialities of faradaic rectification
in the study of fast electrode processes. They also analyzed a variety
of electrode processes. Vdovin also derived the shift of mean poten-
tial in the same way as Barker et al. but independently of the latter
authors. Oldham attacked this problem but his derivation contains
an error which he has since corrected. Further work on theory was done
by Matsuda and Delahay who derived the rectification current-time
dependence for another particular control and analyzed the effect of
the double layer structure. Additional contributions to theory were

5 G. C. Barker, "Square Wave Polarography and some Related Tech-

6 G. C. Barker, R. L. Faircloth and A. W. Gardner, "Use of Faradaic
Rectification for the Study of Rapid Electrode Processes", Nature,

7 G. C. Barker, "Faradaic Rectification", Transactions of the
Symposium on Electrode Processes, Philadelphia, 1959, E. Yeager,

8 Iu. A. Vdovin, "The Theory of the Faradaic Rectification",

9 K. B. Oldham, op. cit.

10 H. Matsuda and P. Delahay, "Faradaic Rectification with Con-
trol of Alternating Potential Variations", J. Am. Chem. Soc., 82,
1547 (1960).
made by Delahay, Senda, and Weis\textsuperscript{11} and by Senda and Delahay.\textsuperscript{12} The work of Fournier\textsuperscript{13} who studied the distortion of polarographic waves upon superimposition of an alternating voltage of relatively large magnitude (perhaps 0.1 Volt) 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 coworkers\textsuperscript{14} (and four previous papers in the series) but these authors did not consider faradaic rectification as discussed below. Application to kinetics was examined by Tachi and collaborators but only for irreversible polarographic waves.

3) \textbf{Qualitative Discussion of Types of Control}

It was noted in the first part of this chapter that there corresponds to an electrode - electrolyte boundary an I-E characteristic. To this relationship then corresponds an impedance. In practice however we can only use an entire cell formed by two electrodes, that is two impedances in series. By making one electrode of an electrolytic cell much larger than the other we render one impedance negligible with respect to the other. Furthermore electrode - electrolyte impedances are more complex than indicated by equation (1-3) because charges on the two sides of the boundary


\textsuperscript{12}M. Senda and P. Delahay, unpublished investigations.


(double layer) form a capacitor. The electrode impedance is better represented by a capacitor (double layer capacity) in parallel with the impedance due to the electrode reaction. The latter is called "faradaic impedance" according to Grahame's\textsuperscript{15} suggestion. These two elements further are in series with the ohmic resistance of the electrolyte and electrodes.

We can in principle control current through the above composite impedance or the voltage applied across this impedance. The control for the faradaic impedance depends furthermore on the relative order of magnitude of $Z_c = 1/\omega C_\varepsilon$ and $Z_f$, where $Z_c$ is the impedance due to double layer capacity $C_\varepsilon$, and $Z_f$ is the faradaic impedance.

Since in faradaic rectification we are dealing with alternating and constant components of potential and current we can have several distinct kinds of control. This can be shown as follows. In the theory of electrical circuits an impedance is defined by

$$Z = \frac{E}{I} \quad (1-6)$$

where $Z$ may be a function of $E$ or $I$. Further, time dependent potential and current can be written as

$$E = E_\infty + E_1 \sin(\omega t + \phi_1) + E_2 \sin(2\omega t + \phi_2) + \ldots \quad (1-7)$$

and

$$I = I_0 + I_1 \sin(\omega t + \phi_1) + I_2 \sin(2\omega t + \phi_2) + \ldots \quad (1-8)$$

In common electrical circuit analysis, in general, \( E \) or \( I \) is imposed and \( I \) or \( E \) is determined. Thus, we are imposing arbitrary values for all \( E_i \) (or \( I_i \)) and having as dependent variables all \( I_i \) (or \( E_i \)). This is what we will call a simple control.

In faradaic rectification practice we will see that it may be more convenient to fix some \( E_i \) and \( I_i \) and have therefore the remaining \( E_j \) and \( I_j \) as dependent variables. This we will call complex control.\(^\text{16}\)

At first let us neglect complications due to the double layer capacity and electrolyte resistance. The types of control across the faradaic impedance of practical realization for faradaic rectification study are of the form of a constant component control (D. Control) associated with an alternating component control (A. Control). The four more important cases are:

Case I

D. _Control_: The mean current through the faradaic impedance, i.e., the D. C. current component, is kept zero \( (\bar{I} = 0) \).
A. _Control_: a sinusoidal alternating current free of harmonics passes through the faradaic impedance (sinusoidal current)

Case II

D. _Control_: as in Case I \( (\bar{I} = 0) \)
A. _Control_: a sinusoidal alternating voltage free of harmonics is applied across the faradaic impedance (sinusoidal voltage)

Case III

D. _Control_: the mean electrode potential, i.e., the D.C. potential component is kept constant and equal to the equilibrium potential \( (E = E_e) \)
A. _Control_: as in case I (sinusoidal current)

\(^{16}\) We are not analyzing the fundamental problem of when and how far this is possible in general. The faradaic rectification theory shows that under certain conditions this seems to be a good approximation of actual faradaic impedance behavior.
Case IV

D. Control: as in case III ($\bar{E} = \bar{E}_e$)
A. Control: as in case II (sinusoidal voltage)

These four cases will be discussed on the assumptions that $E_e = 0$ and that the idealized apparatus of Fig. 1 is used. The case is which $E_e \neq 0$ reduces to the present since an ideal battery can always be assumed to be in series with the cell so that the total voltage is equal to zero at equilibrium. The switches in Fig. 1 are ideal with no switching delay. In all cases the switch is initially in position 2, i.e., the cell is at equilibrium and the voltmeter $V$ reads $\bar{E} = E_e = 0$. The alternating current or potential is then applied by switching from 2 to 1. Two alternate interruptions of the alternating current or potential pulses will be discussed. (1) The cell is short-circuited so that the current resulting from switching back from 1 to 3 can be measured in ammeter $I_1$. (2) The cell circuit is opened to measure any drift of potential.

Case I (Fig. 1a)

Box A represents an ideal sinusoidal current source; $C$ is a sufficiently small blocking capacitor. Turning on the alternating current (2 to 1) will result in the appearance of a rectification voltage i.e., the asymmetry of the faradaic impedance results in a mean potential ($\bar{E}$) across the faradaic impedance. The potential also contains higher harmonics because of the asymmetry of the $I - E$ curve. Since no net current is allowed to flow through the faradaic impedance no net chemical change can occur and there is no gradient of the mean concentrations. Short circuit of the cell (1 to 3) produces no cur-
Fig. 1.-Idealized apparatus for current-potential control in faradaic rectification
rent flow in the circuit of ammeter $I_1$ since no concentration gradient
or associated e.m.f. was developed as a result of the flow of alternating
current. The alternate opening of the cell circuit (1 to 2) results in
an immediate drop of potential from $E_0$ to $E_e = 0$ because no net chemi-
cal change occurred in the cell.

Case II (Fig. 1a)
Box A is now an ideal sinusoidal voltage source. Turning on the alter-
nating voltage (2 to 1) causes the following phenomena. Because of
asymmetry of the $I - E$ curve, an alternating voltage about $E = 0$ would
give rise to a rectified current which is excluded by the blocking
capacitor. However, the electrode behavior is such that an initial
small amount of rectified current produces a small net chemical
change, and charges the blocking capacitor to such a value that an
alternating sinusoidal voltage now about $E \neq 0$ produces a current
free of D.C. but distorted by harmonics. Thus, the turning on of
the alternating voltage causes the mean potential across the faradaic
impedance to change from zero to $E$ almost at once, except for the
charging transient. Short circuit of the cell (1 to 3) produces no
appreciable current flow for the same reason as in Case I. Alternate
opening of the cell circuit (1 to 2) produces an immediate fall of
potential from $E \neq 0$ to $E_e = 0$ for the same reason as in Case I.

Case III (Fig. 1b)
Box B represents an ad hoc A.C. generator such that the alternating
current through the secondary of the transformer is sinusoidal and
free of harmonics. Turning on the alternating current (2 to 1) results
in the following phenomena. Since the current is forced to be sinusoidal, the voltage across the asymmetric faradaic impedance contains higher harmonic terms. There would appear also a rectified voltage but this is excluded (the transformer secondary short circuits the cell for D.C. components) and hence a D.C. component of current will appear \( (I_r) \) to satisfy the \( I - E \) relationship. This produces a net chemical change, and concentration gradients will build up. The change of concentrations at the electrode produces a change in the \( I - E \) relationship such that\(^{17}\) the rectification current \( (I_r) \) tends to decrease with time. Short circuit of the cell \( (1 \text{ to } 3) \) produces a direct current of opposite direction to that of \( I_r \) through the cell owing to the back e.m.f. produced by the concentration gradient. This current decreases with time because of the concentration gradient decay. Alternate opening of the cell circuit \( (1 \text{ to } 2) \) produces a sudden change from mean potential equal to zero to the "rest" potential different of zero. This "rest" potential which is a measure of the preceding concentration gradient build up will now decay with time.

**Case IV (Fig. 1b)**

The Box B represents an ad hoc A.C. generator such that alternating voltage across the secondary is sinusoidal and free of harmonics. Turning on the alternating voltage \( (2 \text{ to } 1) \) produces a current which contains higher harmonic components and also a D.C. component \( (I_r) \). There is a

\(^{17}\)A reason for this can be seen in the Nernst equation or as a consequence of the general principle that a gradient produces a flow tending to decrease the gradient.
net chemical change and the associated concentration gradients. As in Case III the nature of the concentration factors in the $I - E$ relationship is such as to produce a decreasing net current ($I_r$) through the faradaic impedance. Short circuit of the cell (1 to 3) results in an current through the cell opposite to $I_r$ in the same fashion as in Case III. Alternate opening of the cell circuit (1 to 2) produces the corresponding sudden change of potential from mean potential $\bar{E} = 0$ to a "rest" potential different from zero as in Case III.

To summarize and complete 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 $I_r$ which is independent of the type of control of the alternating component harmonics appear 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 harmonics, and only the type 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. This capacity should be as small as feasible to reduce the charging transients. Apparatus for $\bar{E} = E_e$ appear more difficult to realize experimentally and no attempt will be

\[18\text{Same consideration as in footnote 17.}\]
4) Purpose of this Work

The first aim was to develop an instrument fulfilling the conditions required for control of $\bar{I} = 0$ with adequate frequency response. This involved the following two main problems: (1) Rectification voltages of small amplitude with transients of different order of magnitude of time constants must be measured. This requires techniques for low level and low frequencies but wide band measurements. (2) In order to get across the faradaic impedance even a small amplitude alternating signal (a few millivolts) a rather large signal must be applied across the cell owing to the shunting of the faradaic impedance by the low impedance of the double layer capacity. High frequency therefore must be applied to the cell only in short non-recurrent pulses to avoid heating of the solution near the electrode and the concomitant shift of equilibrium potential. Previous work in the field was made either at low frequency (below 50 kilocycles per second) or with a very elaborate instrument (Barker et al.) which did not provide for the study of transients. Theoretical interpretation of results was not as immediate as with the instrument made in this work.

The second aim was to compare experiment with the essential points of a theory previously developed in this laboratory.

Discussion of experimental results will be integrated in the


presentation of theory to avoid repetition and discontinuity in reasoning.
CHAPTER II

EXPERIMENTAL METHODS

1) Solutions

A stock solution of mercurous nitrate in perchloric acid was prepared from analytical grade reagent and purified (to remove traces of adsorbable organic impurities) by treatment with activated charcoal as recommended by Barker.\(^1\) The charcoal was purified by a two-week extraction with boiling hydrochloric acid followed by a one-week extraction with frequently renewed boiling water. Bidistilled water (over potassium permanganate) was used in the preparation of all solutions. A stock solution of perchloric acid was also prepared. The concentration of mercurous ion in the stock solution was determined by electrogravimetry after reduction of any traces of mercuric ion with mercury. The acid solution was titrated.

The Ti (IV) – Ti (III) solutions were prepared from a commercial solution containing approximately 20% titanous chloride. This solution contained, as we found by polarography, an appreciable amount of zinc which however did not interfere. Titanium solutions were prepared in sulfuric and tartaric acid and purified by treatment with charcoal as for the mercurous solution. The purified titanous chloride stock solution was analyzed as follows. An aliquot sample was completely oxidized by hydrogen peroxide and freed almost completely of chloride

---

by treatment with concentrated sulfuric acid and heating to incipient fuming. The sample was then diluted, the titanium reduced back completely to the titanous state by zinc amalgam, and the volume was brought up to a definite value. Finally an aliquot was titrated with permanganate under nitrogen atmosphere.

The Ti (IV) / Ti (III) ratio was changed by complete reduction with zinc amalgam followed by partial oxidation by bubbling of oxygen. For finer control, different amounts of solutions nearly completely reduced and oxidized were mixed. The Ti (IV) / Ti (III) ratio was determined in situ, i.e., in the cell by polarography from the cathodic and anodic diffusion currents. The ratios obtained in this fashion agreed well with the ratios of Ti (IV) / Ti (III) calculated from the equilibrium potentials.

The diffusion coefficients for Ti (IV) and Ti (III) were estimated polarographically: $D_{\text{Ti(IV)}} = D_{\text{Ti(III)}} = 4.4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. This value compares with the value $D_{\text{Ti(IV)}} = 2.9 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ obtained from the polarographic data of Vandenbosch\textsuperscript{2} in a similar medium (10% sulfuric acid and 0.4 molar tartaric acid).

2) Cell

The electrolysis cell used was similar to a conventional polaro-
graphic H-cell. The dropping mercury electrode and the counter electrode, consisting of a mercury pool, were in one arm of the cell. This arm was also provided with inlets and an outlet for passing nitrogen through and over the electrolyte. The other arm of the cell was filled with either 1.0M ammonium nitrate (study of mercurous ion discharge) or 0.88M sulfuric acid (for the Ti(IV) - Ti(III) study). This arm was connected with a salt bridge to a saturated calomel electrode. Precipitation of potassium perchlorate and potassium hydrogen tartrate was thus avoided.

The cell was immersed in a water bath, the water of which made conducting by salt addition was connected to ground. This provided sufficient shielding for the cell.

Nitrogen used for freeing the electrolyte of oxygen was passed over charcoal at dry-ice temperature and brought back to cell temperature by passing it over a portion of same electrolyte as in the cell in a washing bottle.

The dropping mercury electrode capillary was suspended into the cell by means of a plastic foam device and was coupled to the magnetic hammer described below.

3) Instrumentation

A) General Principles

The essential parts and their interconnections are shown in the block diagram of Fig. 2. Their functions are as follows.

a) The Radio Frequency Pulse Path

A radio frequency (R.F.) signal of a chosen frequency is produced continuously by an oscillator (R.F. OSC.). This signal is fed to a gated amplifier (GATE) in order to produce at its output
Fig. 2.—Simplified block diagram of faradaic rectification instrumentation. All sub-assemblies have "ground" as return. Numbers are same as in fig. 3.
only short well defined R.F. pulses. The control of the gate is accomplished by the timing system discussed below.

The R.F. pulses obtained at the gated amplifier output are amplified (R.F. VOLTAGE AMPL.) to a sufficiently high voltage in order to drive the R.F. power output stage (R.F. POWER AMPL.). The R.F. power output stage delivers the pulses at a relatively small voltage but is able to deliver relatively large currents. This output is fed to the cell and is monitored and measured in a suitable oscilloscope (R.F. SCOPE).

The small rectification voltage appearing across the cell is freed from the high frequency pulses in the low pass filter (LOW PASS FILTER) and is measured with a high gain low frequency oscilloscope amplifier (L.F. SCOPE).

b) The Pre-Electrolysis System

For reasons to be described below there is a provision to apply suitably timed constant voltage (D.C.) pulses to the cell. This is achieved by a low resistance battery-potentiometer circuit and suitable mercury relay which switches the D.C. GENERATION sub assembly.

c) The Timing Sequence

The timing sequence is shown in Fig. 3. The principle is to apply the R.F. pulse for a known time interval only once for each drop and this for a known drop area, i.e., for a known drop age. The timing system should also trigger the oscilloscopes since suitable internal triggering would be hard to achieve due to spurious transients due to the fall of the drop. Further it is necessary to observe the potential of the drop before the R.F. pulse is applied since a reference line is
Fig. 3.-Timing sequence for faradaic rectification instrumentation. Order of magnitude of time intervals: $t_0-t_0$, 5 sec., drop time; $t_1-t_0$, 1 sec., age of drop for R.F. pulse; $t_2-t_4$, 10 msec., duration of R.F. pulse; $t_4-t_2$, 1 msec., delay between D.C. generation "off" and R.F. pulse "on"
needed. These objectives are achieved as follows:

A timing CAM begins it cycle by triggering a magnetic HAMMER whose action dislodges the grown drop at the dropping mercury electrode. After a certain fraction of its cycle, the cam triggers a SAWTOOTH GENERATOR.

Excitation of the sawtooth generator produces a short triggering pulse for the oscilloscopes. The sawtooth is fed into three distinct delayed pulse generators (DEL. PULSE A, B, C). Each of this delayed pulse generators produces a output pulse at a given preset fraction of the sawtooth duration. The pulse from delayed pulse generator A is used to switch the gate ON. Later the pulse from the delayed pulse generator B will turn the gate OFF. The delayed pulse generator C produces an output pulse which controls the D.C. generation switching.

B) Details of Block Diagram Sub-Assemblies

 a) The R. F. Generator

For frequencies below 500 kilocycles per second we used a Hewlett-Packard Wide Range Oscillator Mod. #200 CD. For frequencies above 500 kilocycles we used a General Radio o.5-50 MC Unit Oscillator Type #1211-B with suitable separate power supply.

 b) The Gated Amplifier

We began trying several simple self built circuits with gating tubes but we found that they either had not enough gain at the higher frequencies or they gave an excessive pedestal at the output or they did not have an adequate cut-off in the off state. (For principles involved see in for instance Chance.)

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Later we found out that we could use with success the Tektronix Plug-In Unit 53/54 C dual trace calibrated preamplifier. This unit intended for dual trace oscilloscope display consists of two separate input amplifiers connected to a single output by a switching tube. When this unit is set in "Alternate Mode" the switching tube is set into a bistable state. (See manufacturers instruction manual.) One triggering pulse connects one input amplifier to the output while a second triggering pulse switches the output to the other input amplifier. Switching is very fast and pedestals at the output can easily be eliminated by adjustment of the "Vertical Positioning" controls in both inputs. This is because these controls set the D.C. level at the output.

This Tektronix Plug-in unit could have been used in a Tektronix Type 127 Preamplifier power Supply but the output was too low. We adopted the alternative of plugging the 53/54 C unit into a Tektronix Oscilloscope Model 536. We used the output from the "Vertical Signal Out" connector and fed the triggering signals to the oscilloscope time base external triggering connections. The time base had to be set for external triggering and the sweep time had to be set at a value smaller than the time interval between both triggering pulses. Switching proceeded at the beginning of each sweep. The R.F. oscillator output was connected to one of the preamplifier inputs the other input being shorted. In this way the output changed stepwise and at will from zero to a preset value.

A minor inconvenience was associated with the bistability of the switching circuit. When the entire unit was switched on, transients
during the warming up set the switching circuit in one of its positions almost at random. When this was the unwanted alternative, i.e., most of the time non zero output, a simple solution was to switch the mode control back and forth to one of the other modes. This produced switching transients that brought the gating tube to the wanted state. Once this had been done the instrument worked consistently without spurious triggering for any working period.

The maximum output voltage from this arrangement using the Tektronix Type 536 Oscilloscope was approximately 15 volts across a relatively high impedance source and with a band width up to approximately 5 megacycles per second. Since a higher signal level was needed for fully driving the output stage, the signal had to be amplified further almost to one hundred volts.

c) The Radio Frequency Voltage Amplifier

A Tektronix Type 112 Amplifier with a band with up to almost 2 megacycles per second was used to provide an output voltage of about 100 volts.

d) The Radio Frequency Power Output Stage

The aim here was to build a low impedance source able to provide relatively large A.C. currents to a relatively low resistance load (i.e., the electrolytic cell). We built a conventional cathode follower output stage with two 6AS7G triodes in parallel. This tube was selected because of its current carrying capacity and its requirement for a low impedance at optimum load. This output stage had almost the same band-width limitations, i.e., up to 2 megacycles per second, as the previous stage. This stage had its own power supply.
The functions of this part of the circuit (Fig. 4) was to generate in situ one of the components of a redox couple by electrolysis. For this purpose two ganged dropping mercury electrodes were used. Except during the R.F. pulse both electrodes were at the same D.C. potential (with respect to the mercury pool counter electrode) all the time. During the R.F. pulse one of the dropping electrodes (A) was connected to the R.F. source and through a low pass filter to one of the inputs of the low frequency differential preamplifier of an oscilloscope. The other dropping electrode (B) was connected through another low pass filter to the other input of the differential low frequency preamplifier. Rectification voltage were measured as difference between the two potentials (A-B).

Polarization and switching was achieved by a battery and low resistance potentiometer with the help of a fast action low shatter time mercury relay (Western Electric 276B). The mercury relay coil (5000 ohms) was set as anode load of a 6J5 triode circuit. The switching period was imposed on the grid of the triode from the delayed pulse generator C of figure 3.

The hammer was fitted on the movable armature of a 5000 ohm relay. The coil was connected as the anode load of a 6J5 triode. The hammering time pulse generated by a timing cam was applied to the grid circuit.

The timing cam generates the necessary triggering over the long
R.F. POWER OUTPUT

SINGLE HAMMER (RY1)
FOR BOTH CAPIILLARIES
A & B

Fig. 4.-D.C. Generation circuit. R.F. output 4-12 6AS7G in parallel; RY1 hammer: mechanically adapted 5000 ohms relay; RY2 Western Electric mercury relay 276 B; R1 250 ohms; C2 0.003 microfarad; Rh 100 ohms Helipot; L1, C1 and L2, C2 General Radio decade inductors 1490-A and General Radio decade capacitors 1419-K; D.C. scope input, Tektronix model E plug-in differential amplifier; R1 and R2 10 meg-ohms; R.F. scope input (omitted) between A and ground, Tektronix model G plug-in amplifier, Rinput 1 megaohms.
the long period (5 seconds) of the dropping mercury electrode. Two
ganged contact-taster type cams were driven by a synchronous low speed
motor. One revolution of the cam corresponded to the drop time and the
relative position of contacts on the two cams determined the drop age
for which the R,F, pulse formation cycle began. Both cams were part of
separate biasing batteries circuits which provided the proper voltages
to trigger the hammer relay and the sawtooth triggering system.

h) The Sawtooth Generator

A Tektronix Type 162 Waveform Generator, triggered by one of the cams,
was used. Its output pulse triggered the horizontal sweep circuits of
the R,F, and L,F, oscilloscopes. The sawtooth generator also fed three
delayed pulse generators.

i) Delayed Pulse Generators A & B

Tektronix Type 163 Pulse generators were used. Their output was
superimposed through a resistive network and was fed to the gating
amplifier.

j) Delayed Pulse Generator C

This was a Tektronix Type 161 Pulse generator. A single delayed
output pulse of adjustable length was fed to the D,C, generation relay
circuit input to trigger the time and length of the relay action.

k) Low Pass Filter

The low pass filter was set up of General Radio Decade inductors
Type 1490-A (1-1000 mH) and capacitors Type 1419-K (0.001-1. µF.)

l) Low Frequency Oscilloscope Amplifier

A Tektronix Type E Plug-in Unit preamplifier was used at maximum
band with (0.06 c.p.s. - 10 k.c.p.s.). The maximum sensitivity was 0.05
millivolts per cm. At this gain the hum voltage from the complete instrument corresponded to less than 1 cm. peak to peak. Similarly the noise was less than 0.3 cm.

m) Radio Frequency Oscilloscope Amplifier

A Tektronix Type G Plug-in Unit was utilized. This unit has a frequency band width up to 15 MC when used in conjunction with the Tektronix 531 and 535 oscilloscopes.

4) Details on Measurements

a) Cell Resistance

The cell resistance for high frequencies could not be extrapolated from bridge measurements at lower frequencies. Since a high accuracy was not aimed at, the cell resistance was calculated as follows:

A carbon composition resistor of well-known resistance was put in series with the cell. The value of this resistance (R_s) was chosen by trial and error until it was almost equal to the resistance of the cell. R.F. pulses were sent through the circuit and the cell voltage (U_c) and the total voltage (U_t) across the cell plus resistor were measured successively on the R.F. oscilloscope. One had

$$ R_{cell} = R_s \frac{U_c}{(U_t - U_c)} \tag{2-1} $$

By this method the same value of cell resistance was found for all frequency range used (0.05 - 1 MC) and for U_t of very different order of magnitude (0.05 - 2 volts)

b) R.F. Voltage Values

All values reported are amplitudes, i.e., half peak to peak values since we were dealing with sinusoidal voltages. Measurements were made on a calibrated oscilloscope.
c) R.F. Voltage Waveform

The waveform was checked by substitution of a resistor having a similar resistance as the cell for the cell and by the use of long R.F. pulses. A steady wave display was obtained on the oscilloscope (internal triggering) and was compared visually with a sine wave drawn on the screen. At all frequencies used the output was sinusoidal as far as could be ascertained from this visual inspection.

The R.F. waveform was controlled for each measurement from the shape of the R.F. pulse on the R.F. scope. At the low sweep speeds used and for the large frequencies which were selected, the pulse display was similar to a rectangular "raster". Distortion could be detected from a non uniformity of brightness of the rectangular display and from asymmetry about the zero line.

Experience showed that even when distortion was noticeable by these criteria its effect on the rectification voltage was small.

d) Detection of Spurious Rectification

To ascertain whether or not a rectification voltage was really due to an electrode process, the following criteria were adopted: (1) The rectification voltage disappeared when the cell was replaced by a resistor. (2) The rectification voltage remained the same but the polarity was inverted when the cell terminals were switched around. (3) The rectification voltage as read in the oscilloscope was proportional to the sensitivity setting of the oscilloscope. These tests showed that between 0.05 and 1MC, there was no spurious rectification. Above 1MC, criterion 3 was not fulfilled in most experiments for at least one reason, namely that the fraction of the R.F. signal passing
through the low pass filter produced some rectification in the low frequency preamplifier input. A quantitative discussion of this effect is given in Chapter III.

5) Summary of Experimental Conditions

a) The Hg$^2+$ — Hg System

All final solutions were 1.14 molar in perchloric acid and had the following mercurous ion concentration in millimoles per liter:

$#1 - 9.2, #2 - 4.0, #3 - 2.0, #4 - 1.0, #5 - 0.2, #6 - 0.08, #7 - 0.04.$

Cell resistance: 52 ohms (mostly due to the mercury column in the capillary of the dropping mercury electrode).

Mercury height of the dropping mercury: 36.0 cm.

Temperature (30.0 ± 1.0)°C.

Spontaneous drop times: Almost 6 seconds (changed somewhat from solution to solution).

Hammered drop time: 5.02 seconds.

Drop age at beginning of R.F. pulse: 3.7 sec. or 1.3 sec.

Area of drop at 3.7 seconds: $2.06 \times 10^{-2}$ cm$^2$; and at 1.3 seconds

$1.02 \times 10^{-2}$ cm$^2$. (These two times are achieved by simply reversing

of timing cam: $1.3 + 3.7 = 5.0$.)

R.F. pulse length as needed to reach final rectification voltages:

5 to 20 milliseconds.

b) The Ti (IV)/Ti (III) System

Final solutions were all 0.88 molar in sulfuric acid and 0.50 molar in tartaric acid, and 19.5 millimolar in Ti (IV) plus Ti (III). For some especial experiments we used solutions in which the Ti (IV) plus Ti (III)
concentration was either 0.98 millimolar or 1.95 millimolar.

Cell Resistance: 56 ohms.

Rate of flow of mercury: 1.65 mg/sec.

Temperature: (30.0 ± 0.1)°C.

Spontaneous drop time: almost 6 seconds.

Hammered drop time: 5.02 seconds.

Drop age at beginning of R.F. pulse: 3.7 seconds.

Area of drop at 3.7 seconds: \(2.85 \times 10^{-2} \text{ cm}^2\).
CHAPTER III

COMPARISON OF THEORY AND EXPERIMENTAL RESULTS

The sequence of the general treatment of Delahay, Senda and Weis\(^1\) will be followed and experimental results will be integrated in the discussion of theory rather than presented separately. Repetition will be avoided in this fashion.

1) Rectification Voltage and Mean Rectification Current Density.
   
   a. General Correlations

   Non-linearity of the I-E characteristic about \(E_e\) for \(|\gamma| \ll \frac{RT}{nF}\) can be taken into account by inclusion of the terms in \(\gamma^2\) in the expansion of eq. (1-3). The resulting equation has been used by most investigators as the basis for analysis of faradaic rectification just as the linearized I-E characteristic of eq. (1-4) is applied in the treatment of faradaic impedance and other relaxation methods (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 for the methods of faradaic impedance and rectification.

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


31
\[
\left( \frac{nF}{RT} \right) |\delta E| \ll 1, \quad |\delta C_0|/C_0 \ll 1, \quad |\delta C_R|/C_R \ll 1
\]
is written quite generally as
\[
\delta I = \left( \frac{\partial I}{\partial E} \right) \delta E + \left( \frac{\partial I}{\partial C_0} \right) \delta C_0 + \left( \frac{\partial I}{\partial C_R} \right) \delta C_R
\]
where \( \delta \) represent a variation of the quantity being considered and the partial derivatives are expressed at the equilibrium potential \( E_e \). This value of \( \delta I \) is identified with that given by eq. (1-4) in which the partial derivatives are computed from eq. (1-3). The variations \( \delta C_0 \) 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 for the faradaic impedance in terms of these elements of the equivalent circuit of the faradaic impedance, is thus obtained. Particular forms of the faradaic impedance are obtained by introduction of the values of \( \partial I/\partial E, \partial I/\partial C_0 \) and \( \partial I/\partial C_R \) corresponding to the I-E characteristic being selected. Such an approach which was developed by Grahame\textsuperscript{2} for the faradaic impedance has no particular advantage, except perhaps its elegance, over the more direct treatment based on eq. (1-4).

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.

Expressing \( \delta I \) in terms of \( \delta E, \delta C_0, \) and \( \delta C_R \) as for the faradaic impedance but we now include the second partial derivatives of the function \( I = f(E, C_0, C_R) \) to take into account the non-linearity of the I-E

curve about $E_0$. We further note that $\delta I = \sum_{p=0}^{p=2} \delta p I$ where $p = 0, 1,$ and 2 correspond, 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 $(\omega t)^{1/2} \gg 1$. We write for $\delta_p I$

$$\delta_p I = \frac{\partial I}{\partial E} \delta_p E + \frac{\partial I}{\partial C_0} \delta_p C_0 + \frac{\partial I}{\partial C_R} \delta_p C_R + \delta_p^2 I$$  \hspace{1cm} (3-1)

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

$$\delta_p^2 I = \frac{1}{2} \left\{ \frac{\partial^2 I}{\partial E^2} \left[ (\delta_p E)^2 \right] + \frac{\partial^2 I}{\partial C_0^2} \left[ (\delta_p C_0)^2 \right] + \frac{\partial^2 I}{\partial C_R^2} \left[ (\delta_p C_R)^2 \right] \right\} +$$

$$+ \left\{ \frac{\partial^2 I}{\partial E \partial C_0} \left[ \delta_p E \delta_p C_0 \right] + \frac{\partial^2 I}{\partial E \partial C_R} \left[ \delta_p E \delta_p C_R \right] + \frac{\partial^2 I}{\partial C_0 \partial C_R} \left[ \delta_p C_0 \delta_p C_R \right] \right\}$$  \hspace{1cm} (3-2)

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.

One of the mean component $\delta_o I$ or $\delta_o E$ can be controlled, and one generally selects either $\delta_o I = 0$ (mean current equal to zero) or $\delta_o E = 0$ (mean potential equal to equilibrium potential). If $\delta_o I = 0$, there is no net change in the mean concentrations of substances $O$ and $R$, and consequently $\delta_o C_o = \delta_o C_R = 0$ independently of the control of the alternating component (A.C. or A.V. control). One deduces from eq. (3-1)

$$\delta_o E = - \frac{\delta_o^2 I}{\partial I / \partial E}$$  \hspace{1cm} (3-3)

where $-1/(\partial I/\partial E)$ is the charge transfer resistance since there is no net change in the mean concentrations of $O$ and $R$, $\delta_o E$ should be independent of time at least if the double layer capacity is not con-
b) General Equation for the Rectification Voltage.

Application of eq. (3-3) requires the derivation of the explicit form of the quantity $\delta_o \mathbf{I}$ defined by eq. (3-2). The partial derivatives at $E_e$ 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 $\partial^2 \mathbf{I}/\partial C_0^2$, $\partial^2 \mathbf{I}/\partial C_R^2$, and $\partial^2 \mathbf{I}/\partial C_0 \partial C_R$ vanish when the I-E characteristic is of the first order with respect to $C_0$ and $C_R$ since these derivatives are then equal to zero. The quantities $\delta_o E$, $\delta_o C_0$, and $\delta_o C_R$ can be expressed in terms of elements of the equivalent circuit for the electrode reaction (See appendix). If the I-E characteristic of (1-3) holds, the rectification voltage $\Delta E_\infty (\equiv \delta_o E)$, is

$$\Delta E_\infty = \frac{n F}{R T} \nu A \left\{ \frac{2 \alpha - 1}{4} + \frac{\nu_s \left[ (1 - \alpha) \eta_R - \alpha \eta_C \right] + \nu_s \left[ (1 - \alpha) \eta_R - \alpha \eta_C \right]}{2 \left( \nu_s^2 + \eta_s^2 \right)} \right\} (3-4)$$

where $\nu_s$ and $\eta_s$ are the real (resistive) and imaginary (capacitive) components of the series equivalent circuit for the total faradaic impedance per unit area $Z$ ($Z = \nu_F - j \eta_F$, with $j = (-1)^{1/2}$); and $\nu_Q$, $\nu_R$, $\eta_Q$, $\eta_R$ 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.

We use the symbol $\Delta E_\infty$ because $\Delta E$ is a function of time when the double layer capacity is considered and the above value corresponds to $t \to \infty$. One has $\nu_s = \nu_{ct} + \nu_0 + \nu_R$ (3-6) and $\eta_s = \eta_0 + \eta_R$ (3-7), $\nu_{ct}$ being the charge transfer resistance per unit area. Values of the $\nu$'s and $\eta$'s in eq. (3-4) can be taken directly from the classical theory of faradaic impedance.
Equation (3-4) reduces to the result derived by Doss and Agarwall, Barker, Faircloth, and Gardner, and Vdovin for a simple charge transfer reaction. These authors did not write their result in the general form of eq. (3-4) but used the rate constant at the equilibrium potential (not \(k_0\)). They assumed that the current density is \(I_0 \sin t\) and thus postulated implicitly that the mean current is equal to zero. They wrote the potential as \(E_e + \Delta E_\infty = V_A \sin (\omega t - \Theta_a)\) where \(\Delta E_\infty\) 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. (1-3) 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 final equation was solved for \(\Delta E_\infty\).

2) Influence of the Double Layer Capacity for Control of \(I\) at Zero.

a) 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 it is actually

\[\text{References:}\]


the total current density which 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 $C_R$.

The variation of the mean component of the charge $q$ on the
electrode thus is $\delta_q q = (dq/dE) \delta_q E$ or $\delta_q q = c_1 \delta_q E$. (3-8 or 9). 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 $E$. The mean charging current is such that (see eqs. (3-1)
and (3-3))

$$\delta_0 I = \left[ \frac{1}{c_t} \int_0^t \delta_0 I \, dt - \Delta E_{\infty} \right] \frac{\partial I}{\partial E} + \frac{\partial I}{\partial C_0} \delta_0 C_0 + \frac{\partial I}{\partial C_R} \delta_0 C_R$$  \hspace{1cm} (3-10)

The changes in concentrations $\delta_0 C_0$ and $\delta_0 C_R$ can be correlated to
the current density as shown by Delahay, Senda, and Weiss, 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 $\Delta E = \check{\delta}_0 E$ is obtained by integration
of $\delta_0 I$. There follows after substitution of $\partial I/\partial E$, $\partial I/\partial C_0$, and
$\partial I/\partial C_R$ by the corresponding values deduced from eq. (1-3).

$$\Delta E = \Delta E_{\infty} \left\{ \frac{1}{c_t} \frac{\mu F}{RT} \left[ \frac{1}{c} \frac{\sigma}{G} \left( \frac{1}{C_0} D_C^{\nu_1} + \frac{1}{C_R} D_C^{\nu_2} \right) \right] \right\}$$  \hspace{1cm} (3-11)

where $\Delta E_{\infty}$ is given by eq. (3-4) and

$$G, H = \frac{1}{2} \left\{ \left( \frac{I_0^o}{\sigma F} \right) \left( \frac{1}{C_0} D_C^{\nu_1} + \frac{1}{C_R} D_C^{\nu_2} \right) \right\} \left( \frac{1}{\sigma G} \left( \frac{1}{C_0} D_C^{\nu_1} + \frac{1}{C_R} D_C^{\nu_2} \right) \right) \left( \frac{4 I_0^o \sigma F}{RT} \frac{1}{c_0} \right)$$  \hspace{1cm} (3-12)
One can show from eq. (3-11) that $\Delta E = 0$ for $t = 0$ and $\Delta E_\infty \rightarrow \Delta E_i$ for $t \rightarrow \infty$. Mass transfer polarization for the mean concentrations $C_0$ and $C_R$ thus vanishes progressively, and the value $\Delta E_\infty$, as calculated for $I = 0$, is ultimately attained. Further, variations of $\Delta E / \Delta E_\infty$ with time are not affected by frequency. One also can show that $\Delta E = \Delta E_\infty$ for $t > 0$ when $c_1 = 0$ and that $\Delta E = 0$ for $t \rightarrow 0$ when $c_1 \rightarrow \infty$.

Further, one deduces from eq. (3-11) after expansion of the error functions that $\Delta E$ varies linearly with $1/t$ for large arguments, namely

$$\Delta E = \Delta E_\infty \left[ 1 - \frac{RT}{(nF)^2} C_L \left( \frac{1}{C_0 D_0^{1/2}} + \frac{1}{C_R D_R^{1/2}} \right) \frac{1}{(\pi t)^{1/2}} \right] \quad (3-13)$$

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 $\Delta E_\infty$ is practically reached in a short time (perhaps a few milliseconds) for inherently fast reactions and sufficiently concentrated solutions. The time dependence of $\Delta E$ for a given reaction and a given $C^0 + C^0$ also depends on the ratio $C^0 / C^0$ as one would expect from the form of the parameters $G$ and $H$ of eq. (3-12). Finally, $\Delta E / \Delta E_\infty$ for a given $C^0 / C^0$ also depends on $C^0 + C^0$ all other conditions remaining constant (Fig. 5).

The foregoing analysis also holds for the decay curve for $\Delta E$ when the alternating current is interrupted after the limiting value $\Delta E_\infty$ is practically attained. The right-hand member of eq. (3-13) is now equal to $\Delta E_\infty - \Delta E$. This conclusion holds only when $\Delta E_\infty$ is reached at the time of interruption since the previous analysis pre-supposes no mass transfer polarization for the mean concentrations before variation of the alternating current.
Fig. 5.—Variation of $\frac{\Delta \bar{E}}{\Delta E_{\infty}}$ with time according to equation (3-11). Data used in calculations: $D_0=D_R=10^{-5} \text{cm}^2 \text{sec}^{-1}$; $c_1=20$ microfarad cm$^{-2}$; $k_1=1$ cm. sec$^{-1}$; $C_0/C_R=1$. Numbers on curves refer to value of $n^2(C_0+C_R)$. 
The foregoing conclusion that $\Delta \bar{E} / \Delta \bar{E}_\infty$ is independent of $V_A^2$ is strikingly verified in Fig. 6 for the Ti (IV) / Ti (III) charge transfer process. The shape of the $\Delta \bar{E}$ versus time curve is not altered when $\Delta \bar{E}_\infty$ was changed 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 hum and noise at the highest sensitivity.

The conclusion that the $\Delta \bar{E} / \Delta \bar{E}_\infty$ versus t curve is independent of frequency was verified for the discharge of $Hg^{2+}$ on mercury (Fig. 7).

The influence of the concentrations $C_0^0$ and $C_R^0$ on the $\Delta \bar{E} / \Delta \bar{E}_\infty$ versus t curve is shown in Fig. 8 for the Ti (IV) Ti (III) couple. Note that $\Delta \bar{E}_\infty$ is approached more slowly as $[(1/C_0^0 D_0^{1/2}) + (1/C_R^0 D_R^{1/2})]$ increases as one would expect from the simplified equation (3-13).

b. Rectification from the Double Layer.

The foregoing analysis will now be modified to take into account rectification due to the double layer capacity. As was shown by Barker, variations of the differential capacity $c_1$ of the double layer with potential results in a shift of the mean potential

$$\Delta \bar{E}_c = \frac{1}{4 c_e} \frac{d c_e}{d E} V_A^2 \quad (3-14)$$

where $V_A$ is the amplitude of the alternating voltage across $c_1$. The shift $\Delta \bar{E}_c$ is frequency independent and if $(1/c_1)(d c_1/d E)$ does not

---

Fig. 6.- Tracings of oscillograms of $\Delta E$ versus time for Ti(IV)/Ti(III) in 0.88 M sulfuric acid and 0.50 M tartaric acid, 1.4 ml Ti(IV) and 18.8 ml Ti(III). Data obtained with the following filter components: $C=0.5$ microfarad, $L=10$ millihenries. Oscillatory transients omitted.
Fig. 7.-Tracings of oscillograms of $\Delta E$ versus time for discharge of 0.08 mM Hg$^{2+}$ in 1.14 M perchloric acid for different frequencies.
Fig. 8.—Tracings of oscillograms of $\frac{\Delta E}{\Delta E_\infty}$ versus time for Ti(IV)/Ti(III) in 0.88 M sulfuric acid and 0.50 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 $(1/C_0 D_C^2)/(1/C_0 D_R^2)$ in $10^8$ sec$^{-1}$ mol$^{-1}$ cm$^2$ for curves 1 to 5: 1.1, 2.8, 4.0, 11.4, 12.0 for $D_C = D_R = 0.44 \times 10^2$ cm$^2$ sec$^{-1}$. $\Delta E$ and $\Delta E_\infty$ were positive for curve 2 and negative for the other curves.
depend on frequency. This seems to be so for frequencies studied thus far, i.e., up to 1-2 megacycles per sec.

If there is a charge transfer reaction, the net shift of mean potential is a combination of the shift of potential of eq. (3-13) and $\Delta E_1$ of eq. (3-14). The term between brackets in eq. (3-10) now includes $\Delta E_1$, and eq. (3-11) is replaced by

$$
\Delta E = \Delta E_\infty - \left( \Delta E_\infty - \Delta E \right) \frac{1}{\zeta_\infty} \frac{\eta^F}{R T} \frac{1}{\xi - H} \left[ \frac{1}{\eta} \exp \left( \xi^H t \right) \exp \left( \eta^H t \right) \right]
$$

(3-15)

There follows that $\Delta E = \Delta E_1$ at $t = 0$, and $\Delta E = \Delta E_\infty$ for $t \to \infty$.

The shift of mean potential upon interruption of the alternating current when $\Delta E_\infty$ is practically reached is $-\Delta E_1$.

These conclusions from theory are borne out experimentally as Fig. 7 shows.

3) **Rectification Voltage in the Absence of Coupled Chemical Reaction**

   **a. Influence of Applied Voltage.**

   The general equation (3-4) for the rectification voltage can be written after introduction of the $r$'s and $y$'s from faradaic impedance theory in the form:

$$
\Delta E_\infty = \frac{n F}{R T} V_0^2 \left( \frac{2\alpha - 1}{4} - \frac{1}{2} \left[ \alpha - \frac{C_0 D_0 V_0^2}{C_0 D_0 V_0^2 + C_R D_R V_0^2} \right] \right)
$$

(3-16)

where $\Theta_a$ is the phase shift between current and voltage as derived in the faradaic impedance theory.

It follows that $\Delta E_\infty = 0$ when $C_0 D_0 V_0^2 = C_R D_R V_0^2$ and $\alpha = 0.5$, as one would expect. One also infers from eq. (3-16) that $\Delta E_\infty$ is proportional to $V_0^2$. If the cell resistance is much larger than the
combined impedance of the faradaic impedance in parallel with the double layer capacity, $\Delta E_\infty$ is also proportional to the square of the cell voltage.

These two proportionality relationships were always verified experimentally for the Ti (IV) - Ti (III) couple and the Hg (I) discharge. Some experimental results are given in Fig. 9 and Table I. 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. cm$^{-2}$ (Table II). It is to be noted that $\Delta E_\infty$ is proportional to $V_A^2$ for values of $V_A$ exceeding 50 millivolts whereas it was assumed in the theory that $V_A$ does not exceed a few millivolts. Third order effects must, therefore, be quite negligible.

b) Influence of Frequency

The effect of frequency on $\Delta E_\infty$ was examined by Barker only briefly and in greater detail by Delahay, Senda, and Weis. Two terms in equation (3-16) must be considered, namely $V_A$ and $\text{ctn} \Theta_A$.

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 $\omega \to 0$ and control by kinetics of

---


Fig. 9. Variations of $\Delta E_{\infty}$ with the cell R.F. voltage (log-log plot) for 0.7 M Ti(IV) plus 18.8 M Ti(III) in 0.88 M sulfuric acid and 0.50 M tartaric acid at different frequencies (in megacycles per sec.).
TABLE I

Variation of $\Delta \bar{E}_\infty$ with $V_A$ for 0.7 mM Ti(IV) plus 18.8 mM Ti(III) in 0.88 M $H_2SO_4$ and 0.50M tartaric acid at different frequencies.

<table>
<thead>
<tr>
<th>$f$ M.C.</th>
<th>$U_A$ VOLTS</th>
<th>$-\Delta \bar{E}_\infty$ mV.</th>
<th>$V_A$ mV.</th>
<th>$-\Delta \bar{E}_\infty/V_A^2$ VOLTS/VOLTS²</th>
</tr>
</thead>
<tbody>
<tr>
<td>.01</td>
<td>.040</td>
<td>.42</td>
<td>15.</td>
<td>1.93</td>
</tr>
<tr>
<td>.075</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.02</td>
<td>.070</td>
<td>.27</td>
<td>13.</td>
<td>1.63</td>
</tr>
<tr>
<td>.13</td>
<td>1.0</td>
<td>24.</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>.20</td>
<td>2.4</td>
<td>37.</td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td>.05</td>
<td>.19</td>
<td>.30</td>
<td>14.</td>
<td>1.52</td>
</tr>
<tr>
<td>.29</td>
<td>.80</td>
<td>22.</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>.48</td>
<td>2.3</td>
<td>36.</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>.90</td>
<td>7.0</td>
<td>67.</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>.1</td>
<td>.36</td>
<td>.28</td>
<td>13.</td>
<td>1.57</td>
</tr>
<tr>
<td>1.1</td>
<td>2.6</td>
<td>40.</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>12.</td>
<td>85.</td>
<td>1.66</td>
<td></td>
</tr>
<tr>
<td>.2</td>
<td>.48</td>
<td>.20</td>
<td>8.8</td>
<td>2.57</td>
</tr>
<tr>
<td>1.4</td>
<td>1.0</td>
<td>26.</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>2.8</td>
<td>40.</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>6.4</td>
<td>63.</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>.5</td>
<td>1.2</td>
<td>.14</td>
<td>8.9</td>
<td>1.82</td>
</tr>
<tr>
<td>2.1</td>
<td>.36</td>
<td>16.</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>1.3</td>
<td>30.</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>4.0</td>
<td>48.</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
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<td>1.6</td>
<td>.05</td>
<td>5.9</td>
<td>1.43</td>
</tr>
<tr>
<td>3.6</td>
<td>.24</td>
<td>13.</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>.8</td>
<td>18.</td>
<td>2.54</td>
<td></td>
</tr>
</tbody>
</table>
TABLE II

Differential capacity of the supporting electrolyte (0.88 M H₂SO₄ & 0.50 M tartaric acid) for the Ti(IV) / Ti(III) system at 250 cycles per sec.

<table>
<thead>
<tr>
<th>E (Volts vs. S.C.E.)</th>
<th>C₁ (µEcm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.050</td>
<td>31.6</td>
</tr>
<tr>
<td>-0.100</td>
<td>30.4</td>
</tr>
<tr>
<td>-0.150</td>
<td>29.4</td>
</tr>
<tr>
<td>-0.200</td>
<td>28.6</td>
</tr>
<tr>
<td>-0.250</td>
<td>28.0</td>
</tr>
<tr>
<td>-0.300</td>
<td>27.1</td>
</tr>
<tr>
<td>-0.350</td>
<td>26.8</td>
</tr>
<tr>
<td>-0.400</td>
<td>25.5</td>
</tr>
<tr>
<td>-0.450</td>
<td>24.5</td>
</tr>
<tr>
<td>-0.500</td>
<td>23.4</td>
</tr>
<tr>
<td>-0.550</td>
<td>22.4</td>
</tr>
<tr>
<td>-0.600</td>
<td>21.6</td>
</tr>
<tr>
<td>-0.650</td>
<td>-</td>
</tr>
<tr>
<td>-0.700</td>
<td>20.6</td>
</tr>
<tr>
<td>DROP AGE</td>
<td>DROP AREA</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td>1.02 x 10^{-2} cm^{2}</td>
</tr>
<tr>
<td>( \dot{f} )</td>
<td>( U_A )</td>
</tr>
<tr>
<td>MC (Volts)</td>
<td>mV</td>
</tr>
<tr>
<td>0.15</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>0.145</td>
</tr>
<tr>
<td>0.30</td>
<td>0.11</td>
</tr>
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<td></td>
<td>0.19</td>
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<td></td>
<td>0.24</td>
</tr>
<tr>
<td>0.60</td>
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</tr>
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<td></td>
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</tr>
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<td>1.00</td>
<td>0.40</td>
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<tr>
<td></td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
</tr>
<tr>
<td>1.50</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
</tr>
</tbody>
</table>
charge transfer for $\omega \to \infty$. One has $\text{ctn} \Theta_a \to 1$ for diffusion control and

$$\left( \frac{\Delta E_\infty}{V^2_A} \right)_{\omega \to 0} = \frac{nF}{4RT} \left( \frac{C^0_D D^{\frac{1}{2}}_0 - C^0_R D^{\frac{1}{2}}_R}{C^0_D D^{\frac{1}{2}} + C^0_R D^{\frac{1}{2}}_R} \right) \quad (3-17)$$

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, $\Delta E_\infty / I^2_A$ 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 $1/\omega^{\frac{1}{2}}$ for a diffusion-controlled process, and $\Delta E_\infty / I^2_A$ is proportional to $1/\omega$.

If $\omega \to \infty$, one has $V_A \to 0$ for any finite $I_A$, and consequently $\Delta E_\infty \to 0$. Further,

$$\left( \frac{\Delta E_\infty}{V^2_A} \right)_{\omega \to \infty} = \frac{nF}{4RT} (2\alpha - 1) \quad (3-18)$$

At sufficiently high frequencies, $\Delta E_\infty / V^2_A$ varies linearly with $1/\omega^{\frac{1}{2}}$. 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

$$\frac{1}{\text{ctn} \Theta_a} = \frac{I^0_a}{2^{\frac{1}{2}} nF} \left( \frac{1}{C^0_D D^{\frac{1}{2}}_0} + \frac{1}{C^0_R D^{\frac{1}{2}}_R} \right) \frac{1}{\omega^{\frac{1}{2}}} \quad (3-19)$$

provided that $\omega^{\frac{1}{2}} \gg 10^3 I^0_a \cdot (D^0_0 = D^0_R = 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1}, C^0_0 = C^0_R)$. Under these conditions, $\Delta E_\infty / V^2_A$ varies linearly with $1/\omega^{\frac{1}{2}}$.

The transfer coefficient $\alpha$ is obtained from the intercept at $1/\omega^{\frac{1}{2}} = 0$ and $I^0_a$ is then calculated from the slope of this plot. As a verification, $\alpha$ can also be determined from the variations of $I^0_a$ with reactant concentration.

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. 11 for the discharge of Hg (I) on mercury confirm these conclusions. At low mercurous ion concentrations the condition $1/\omega c_1 \ll Z$ is approached, and $\Delta \bar{E}_\infty / I_A^2$ should and is proportional to $1/\omega^2$. Conversely at higher mercurous ion concentrations the condition $1/\omega c_1 \gg Z$ is approached, and $\Delta \bar{E}_\infty / I_A^2$ should and does approach the $1/\omega$ dependence.

On the other hand at lower concentrations

$$(\Delta \bar{E}_\infty / I_A^2)_{\omega \to 0} \to k (\Delta \bar{E}_\infty / V_A^2)_{\omega \to 0}$$

become independent of the mercurous ion concentration since

$$C_o D_o^{-1/2} \ll C_R D_R^{-1/2} \quad (3-20)$$

and the second fraction in equation (3-17) should approach the value one. This is consistent with the experimental observation that in Fig. 11 the curves for 0.2, 0.08 and 0.04 mM Hg$^2^+$ coincide within experimental error.

Extrapolation of $\Delta \bar{E}_\infty / V_A^2$ to $\omega = 0$ for the data at concentrations of 0.2, 0.08 and 0.04 mM Hg$^2^+$ gave the limiting value $\Delta \bar{E}_\infty / V_A^2 = \pm 5$ volt$^{-1}$ for an assumed differential capacity of 160 microfarad cm$^{-2}$. This is the limiting value $n F / 4 R T$ for $n = 2$ in this case. No accurate verification was possible because the double layer capacity cannot be measured in this case.

Variations of $\Delta \bar{E}_\infty / V_A^2$ with the ratio $C_0^0 / C_R^0$.

Variations of $\Delta \bar{E}_\infty / V_A^2$ with the ratio $C_0^0 / C_R^0$, i.e., with the equilibrium potential, were also examined. This analysis is directly
Fig. 10.—Plot of $\log(\Delta E_\infty/I_A^2)$ versus $\log\omega$ for the discharge of $\text{Hg}^{2+}$ at different concentrations (mM per liter) in 1.14 M perchloric acid. $\Delta E_\infty$ was negative for all concentrations.
Fig. 11. - Plot of \( \frac{4RT}{nF}(\Delta E_{\infty}/V_A^2) \) against \( \frac{nF}{RT}(E_e-E_{V/2}) \) for different values of \( k_a/(2\omega D) \), D being the common value of \( D_0 \) and \( D_R \). \( \alpha = 0.25 \). Values of \( k_a/(2\omega D) \) for curves 1 to 9: \( \infty, 1, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, \) zero.
derived from that of Barker\textsuperscript{11} who considered $\Delta \bar{E}_\infty$ (which vanishes for $\omega \to \infty$) rather than $\Delta \bar{E}_\infty / V_A^2$. Two limiting cases will be considered: $\omega \to 0$ and $\omega \to \infty$ for which eqs. (3-17) and (3-18) apply, respectively. 

\[
\Delta \bar{E}_\infty / V_A^2 \text{ for } \omega \to 0 \text{ varies with }
\]

\[
(C_0 D_o V_2^- - C_R D_R V_2^-) / (C_0 D_o V_2^+ + C_R D_R V_2^+)
\]

This quantity approaches $\pm 1$ for $E_e \to \pm \infty$ and is equal to zero for $E_e = E_{v2}$. Hence $\Delta \bar{E}_\infty / V_A^2 = \pm nF/4RT$ for $E_e \to \pm \infty$ and $\omega \to 0$. Equation (3-17) applies for $\omega \to \infty$, and $\Delta \bar{E}_\infty / V_A^2 \geq 0$ for $\alpha > 0.5$. 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. 11). All curves intersect at the point having the ordinate $\Delta \bar{E}_\infty / V_A^2 = (nF/4RT)(2\alpha - 1)$ and the abscissa such that

\[
\tan\left[\frac{1}{2} \frac{nF}{R T} (E_e - E_{v2})\right] = (2\alpha - 1) \quad (3-21)
\]

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

Experimental curves for the Ti(IV) - Ti(III) couple in Fig. 12 have the same general shape as the theoretical curves of Fig. 11, and exhibit a single intersection point. The values $\alpha_c = 0.25$ and $\alpha_c = 0.46$ were calculated from the abscissa and ordinate respectively, of the intersection point. No conclusive interpretation can be given for this discrepancy but at least two possible explanations can be offered:

\textsuperscript{11}The same as note 9 in this chapter.
Fig. 12.-Plot of $\frac{\Delta E_{\alpha}/V^2}{V_A}$ against $C_{\text{Ti(IV)}}/C_{\text{Ti(III)}}$ for Ti(IV)-Ti(III) in 0.88 M sulfuric acid and 0.50 M tartaric acid for different frequencies (in megacycles per sec.).

$C_{\text{Ti(IV)}} + C_{\text{Ti(III)}} = 19.5$ mM
the influence of absorbed tartaric acid which complicates the interpretation of the charge transfer process, and the possibility of a chemical reaction preceding or following the charge transfer reaction.

4) 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 \( \Delta E_\infty \) 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 \( I_0 \)'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 percent for \( t > 5 r c \), \( r \) being the total resistance of the circuit connected to the alternating current generator and \( c_r \), for control of \( I = 0 \), the capacity equivalent to the series combination of the double layer differential capacity and the capacity in series with the cell (Blocking capacitor). The latter capacity which generally need 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 \( r \) (\( r = 100 \) 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 $\Delta \overline{E}_\infty$. Since $|\Delta \overline{E}_\infty| \leq (nF/4RT)V_A^2$ and $V_A \leq 0.005$ volts, one has $|\Delta \overline{E}_\infty| \approx 100$ to 200 microvolts. Further $|dE_e/dt| \leq 1$ milivolt degree$^{-1}$ in general, and consequently one should have $\Delta T \leq 0.001$ 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 $dT/dt = 0.24 (I_A^2/2) (1/\kappa_e \sigma_e C_h)$ at the electrode surface, $\kappa_e$ being the specific conductance of the electrolyte, $C_h$ its specific heat, and $\sigma_e$ its density. For instance, for a 1 molar aqueous solution of a strong acid one has at room temperature $dT/dt = 0.3 I_A^2$ degrees sec.$^{-1}$ or for $I_A = 1$ amp. cm.$^2$ (an order of magnitude for $f = 1$ megacycle per sec.), $dT/dt \approx 0.3$ degrees sec.$^{-1}$ Since one should have $\Delta T \leq 0.001$ to 0.01 degree, $\Delta \overline{E}_\infty$ 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 $\Delta \overline{E}_\infty$ by means of a low pass filter. Requirements for this filter become more stringent as the resistance increases as one can readily show. Let $U$ (Fig. 13) represent the total voltage composed of a low frequency component $\overline{E}$ (including D.C.) and a high frequency component $V$. "Low" and "high" here are relative to the filter
Fig. 13.—Diagram for discussion of filter limitations
cut off frequency. The low pass filter behavior can be described with an approximation enough for our purpose by

\[ E_{\text{out}} = E_{\text{in}} \]  

(3-22)

and

\[ V_{\text{out}} = \left( \frac{\omega}{\omega_0} \right)^m V_{\text{in}} \]  

(3-23)

for \( \omega_0 \) being the cut-off frequency. For a simple L-C low pass filter \( m = 2 \). The faradaic rectification voltage can be written as

\[ E_{\text{in}} = k_R \frac{1}{R_c \omega^2} V_{\text{in}}^2 \]  

(3-24)

The condition for avoiding spurious rectification in the detector and saturation of the amplifier is

\[ \frac{E_{\text{out}}}{V_{\text{out}}} \gg 1 \]  

(3-25)

By combination of equations (3-22), (3-23), and (3-24) there results

\[ \frac{E_{\text{out}}}{V_{\text{out}}} = k_R \frac{\omega^{(m-2)}}{R_c \omega_0^m} V_{\text{in}} \]  

(3-26)

Equation (3-26) shows clearly how attainment of condition (3-25) is adversely affected by high cell resistance. Equation (3-26) also gives a simple basis for study of the factors controlling the filter efficiency.

5) Generation of One Reactant in Situ

The ratio \( C_0^\circ / C_R^\circ \) of the concentrations of the oxidized to reduced species can be adjusted as was done for the Ti(IV)Ti(III) system by control of the bulk concentrations of substance 0 and R. Much labor would be avoided if one of the species could be prepared in situ by
polarographic technique. Such a method is applied in A.C. polarography and it was first applied by Randles and White\textsuperscript{12} in faradaic impedance measurements for the discharge of Ni (II) in molten salts.

In faradaic rectification with control at $\bar{I} = 0$, generation must be interrupted because the D.C. resistance across the cell must, in principle, be infinite. The necessary instrumentation was developed as discussed in Chapter II, (D.C. GENERATION SUB ASSEMBLY). Results were not satisfactory because the ratio $C^0_0 / C^0_R$ built up by pre electrolysis decayed rapidly, and the rectification voltage was superimposed on the drifting equilibrium potential. Theoretical interpretation of this transient is difficult because of convection at the electrode (cf. theory of polarographic maxima). Further the potential difference between drops and counter electrode (see Fig. 4) was so large as to overcome the rejection ratio of the differential amplifier for a common mode signal.

Generation therefore appears quite difficult in the method with control of $\bar{I} = 0$.

1) Potentialities of the Method

The faradaic rectification method appears as a most promising tool for the study of fast electrode processes. Results obtained in this investigation show that the electrode behavior can be studied at very high frequencies under conditions which compare favorably with other relaxation methods. Comparison will be limited to the potentialities in the study of fast electrode processes, and features which might be of significance in the study of surface phenomena (crystallization, surface coverage, etc.) will not be considered.

Limitations imposed by the ohmic drop and the double layer capacity which were discussed by Delahay\(^1\) for each relaxation method are largely eliminated in the application of faradaic rectification to very fast reactions. The 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 \(\Delta E\) 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 $k_a^0$ which could be determined can be set only after further evaluation but it appears that values of $k_a^0$ up to 10 or to 100 cm.sec.$^{-1}$ could be measured. This upper limit is based on the assumption that frequencies up to 100 megacycles per second can be used.

2) Suggestions for Further Work

The potentialities of faradaic rectification can be fully exploited only if an instrument operating at frequencies above 1 megacycle per second is available. This will require some change in present instrumentation now available in this laboratory. Amplifiers, especially power stages, at very high frequencies begin to fail and one would have to change to tuned stages using techniques similar to those of radio frequency transmitters. This change seems to offer, in principle, no essentially new difficulty. Further a more serious problem may result from the necessity of using very short pulses to avoid heating of the solution. Finally, the question arises, at very high frequencies whether formulae 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.$^2$.sec.$^{-1}$) for $t = 10^{-8}$ sec. is still quite large in comparison with molecular dimensions.

It may be concluded that in its present stage of development faradaic rectification should prove particularly useful for the study of charge transfer processes without and with coupled chemical reaction. Application to the study of double layer effects and partic-
ularly to non-Frumkin corrections of the type analyzed in this Labora-
tory should be of great interest. New knowledge should also be gained
by application to absorption at electrodes of ions and neutral species
in view of its very high frequencies which can be explored.
APPENDIX

As noted in Chapter III equation (3-4) is deduced from equation (3-3) in which $\zeta_0^2 I$ is derived from equation (3-2). Further the terms in $\frac{\partial^2 I}{\partial C_R^2}$, $\frac{\partial^2 I}{\partial C_O^2}$, and $\frac{\partial^2 I}{\partial C_R \partial C_O}$ in equation (3-2) vanish if we assume, as will be the case here, that the I-E characteristic is linear in the concentrations of 0 and R (cf. eq. 1-3). The problem thus is to express $\zeta_0 C_O$ and $\zeta_1 C_R$ of equation (3-2) in terms of the resistive and capacitive elements of the series equivalent circuit for the faradaic impedance. The following treatment is due to Delahay, Senda, and Weis.

Quite generally one has with the conventions of sign for equation (1-3)

$$\sigma I = - \frac{\sigma E}{r_s - \partial y_s} \quad (A-1)$$

where $r_s$ and $y_s$ are the resistive and capacitive elements of the series equivalent circuit for the faradaic impedance (cf. eq. 1-3 3-6 and 3-7). Further, if we assume that the kinetic parameters for the supply and/or removal of 0 and R (diffusion, homogeneous or heterogeneous chemical reaction, etc.) are independent of potential, one has for species $i$ ($\Xi 0$ or $R$)

$$\sigma_i C_i = \pm \left[ (h_{x_i})_i - \gamma (h_{y_i})_i \right] \sigma_i I \quad (A-2)$$

where the sign hold for 0 and R respectively, and $h_{x_i}$ and $h_{y_i}$ are constants which depend only on the processes for supply and/or
removal of $0$ and $R$ between the bulk of solution and the electrode

By introduction of $\delta_1 C_i$ from equation (A-2) into

$$\delta_1 I = \frac{\partial I}{\partial E} \delta_1 E + \frac{\partial I}{\partial C_0} \delta_1 C_0 + \frac{\partial I}{\partial C_R} \delta_1 C_R \quad (A-3)$$

one obtains after re-arrangement of terms

$$\delta_1 I = \frac{-\delta_1 E}{\frac{1}{\partial E} + \frac{\partial C_R}{\partial E}(k_R) - \frac{\partial C_O}{\partial E}(k_O) - \frac{\partial C_R}{\partial E}(k_R) - \frac{\partial C_O}{\partial E}(k_O)}$$

or

$$\delta_1 I = \frac{-\delta_1 E}{\eta_{ct} + \eta_R + \eta_0 - \gamma (\eta_R + \eta_0)} \quad (A-5)$$

where $r_{ct}$, $r_R$, $r_0$, $y_R$, $y_0$ are defined in conjunction with equations (3-6) and (3-7). The values of the $r$'s and $y$'s are readily written by comparison of equations (A-4) and (A-5).

By introducing in equation (A-2) the $r$'s and $y$'s thus obtained one derives for species $i$ ($i \equiv 0$ or $R$)

$$\delta_1 C_i = \left[ \frac{\partial I}{\partial E} \right] \left[ \frac{\partial I}{\partial C_i} \right] (\eta_0 - \gamma \eta_s) S_1 I \quad (A-6)$$

or after combination with equation (A-1)

$$\delta_1 C_i = -\left[ \frac{\partial I}{\partial E} \right] \left[ \frac{\partial I}{\partial C_i} \right] \left( \frac{\eta_0 - \gamma \eta_s}{\eta_0 - \gamma \eta_s} \right) S_1 E \quad (A-7)$$

A general equation for $\delta_0 I$ of equation (3-3) can thus be written from equations (3-2) and (A-7). Equation (3-4) was derived by substitution of the following values corresponding to equation
(1-3) for the partial derivatives at $E_e$:

\[
\begin{align*}
\frac{\partial I}{\partial E} &= - I_\alpha^0 (n F/RT), \\
\frac{\partial I}{\partial C_0} &= I_\alpha^0 / C_0^0, \\
\frac{\partial I}{\partial C_R} &= - I_\alpha^0 / C_R^0, \\
\frac{\partial^2 I}{\partial E \partial E} &= - I_\alpha^0 \left[ (1-\alpha)^2 - \alpha^2 \right], \\
\frac{\partial^2 I}{\partial E \partial C_0} &= - (I_\alpha^0 / C_0^0) (\alpha n F/RT), \\
\frac{\partial^2 I}{\partial E \partial C_R} &= - (I_\alpha^0 / C_R^0) [(1-\alpha) n F/RT], \\
- (\frac{\partial I}{\partial E}) / (\partial I / \partial C_0) &= (n F/RT) C_0^0, \\
\text{and finally} \\
- (\frac{\partial I}{\partial E}) / (\partial I / \partial C_R) &= - (n F/RT) C_0^0.
\end{align*}
\]
SELECTED BIBLIOGRAPHY


VITA

Carl Herrmann Weis was born November 8, 1928 in Porto Alegre, R.G.S., Brazil. He there received his elementary and secondary education which was completed in 1947.

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