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Faradaic Rectification and Electrode Processes.

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FARADAIC RECTIFICATION

AND

ELECTRODE PROCESSES

A Dissertation

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in

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by

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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 $\text{Ti(IV)} - \text{Ti(III)}$ 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

¹P. Delahay, "The Study of Fast Electrode Reactions by Relaxation Methods", Chapter 5 in "Advances in Electrochemistry and Electrochemical Engineering", P. Delahay and C. W. Tobias, editors, Interscience Publishing Co., New York, in course of publication.

We consider a simple electrode reaction corresponding to the equation

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

$$I = I_a^0 \left\{ \exp \left[- \frac{\alpha n F}{R T} \eta \right] - \exp \left[\frac{(1-\alpha) n F}{R T} \eta \right] \right\} \quad (1-2)$$

where I_a^0 is the apparent exchange current density, a parameter of the reaction kinetics; α , the transfer coefficient, a second parameter necessary to characterize the reaction kinetics; η 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

$$I = I_a^0 \left\{ \frac{C_O}{C_O^0} \exp \left[- \frac{\alpha n F}{R T} \eta \right] - \frac{C_R}{C_R^0} \exp \left[\frac{(1-\alpha) n F}{R T} \eta \right] \right\} \quad (1-3)$$

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

$$-\left(\frac{\partial \eta}{\partial I} \right)_{I \rightarrow 0} = \frac{R T}{n F} \left[- \frac{1}{C_O^0} \left(\frac{\partial C_O}{\partial I} \right)_{I \rightarrow 0} + \frac{1}{C_R^0} \left(\frac{\partial C_R}{\partial I} \right)_{I \rightarrow 0} + \frac{1}{I_a^0} \right] \quad (1-4)$$

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 relationship is not linear and is not necessarily symmetrical, i.e.,

$$I(\eta) \neq I(-\eta) \quad (1-5)$$

non-linearity and asymmetry of this current density-potential curve causes rectification as is well known from the study of I - E characteristics 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 Agarwall² who designated it as the „redoxokinetic" effect. The expression „faradaic rectification" used here was coined by Oldham.³ Doss and Agarwall⁴ derived the shift of mean potential for a particular control in the

²K.S.G. Doss and H. P. Agarwall, "A New Polarization Effect: Redoxokinetic Potential", J. Sci. Industr. Res. India 9B, 280 (1950).

³K. B. Oldham, "Faradaic Rectification: Theory and Applications to the $\text{Hg}_2^{+2}/\text{Hg}$ Electrode," Trans. Faraday Soc. 53, 80 (1957).

⁴K.S.G. Doss and H. P. Agarwall, "The Theory of the Redoxokinetic Effect and a General Method for the Determination of α of absolute Reaction Rates," Proc. Indian Acad. Sci., 34A, 263 (1951).

special case of reactants and products having equal concentrations and diffusion coefficients. These authors also pointed out the applications to kinetics. Barker, Faircloth, and Gardner⁵⁻⁷ 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. Vdovin⁸ also derived the shift of mean potential in the same way as Barker et al. but independently of the latter authors. Oldham⁹ attacked this problem but his derivation contains an error which he has since corrected. Further work on theory was done by Matsuda and Delahay¹⁰ 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

⁵G. C. Barker, "Square Wave Polarography and some Related Techniques", Anal. Chim. Acta, **18**, 118 (1958).

⁶G. C. Barker, R. L. Faircloth and A. W. Gardner, "Use of Faradaic Rectification for the Study of Rapid Electrode Processes", Nature, **181**, 247 (1958).

⁷G. C. Barker "Faradaic Rectification", Transactions of the Symposium on Electrode Processes, Philadelphia, 1959, E. Yeager, editor, Wiley, New York, 1960.

⁸Iu. A. Vdovin, "The Theory of the Faradaic Rectification", Doklady Akad. Nauk S.S.S.R., **120**, 554 (1958).

⁹K. B. Oldham, op. cit.

¹⁰H. Matsuda and P. Delahay, "Faradaic Rectification with Control of Alternating Potential Variations", J. Am. Chem. Soc., **82**, 1547 (1960).

made by Delahay, Senda, and Weis¹¹ and by Senda and Delahay.¹² The work of Fournier¹³ 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 coworkers¹⁴ (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) 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

¹¹P. Delahay, M. Senda, and C. H. Weis, "Faradaic Rectification and Electrode Processes", J. Am. Chem. Soc., in course of publication.

¹²M. Senda and P. Delahay, unpublished investigations.

¹³M. Fournier, "Influence de la frequence de la tension appliquee a une electrode a goutte de mercure. Etude des courbes polarographiques," Compt. rend. Acad. Sci. Paris, **232**, 1673 (1951).

¹⁴M. Senda and I. Tachi, "Studies on A. C. Polarography. V. Theory of Reversible Wave", Bull. Chem. Soc. Japan, **28**, 632 (1955).

(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's¹⁵ 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 $Z_c = 1/\omega C_\ell$ and Z_f where Z_c is the impedance due to double layer capacity C_ℓ , 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

$$E = E_0 + E_1 \sin(\omega t + \psi_1) + E_2 \sin(2\omega t + \psi_2) + \dots \quad (1-7)$$

and

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

¹⁵D. C. Grahame, "Mathematical Theory of Faradaic admittance (Pseudocapacity and Polarization Resistance)", J. Electrochem. Soc. **99**, C370 (1952).

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.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)

¹⁶We 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 ($\bar{E} = E_e$)

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 in 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 $\bar{E} = 0$ to $E_e = 0$ because no net chemical change occurred in the cell.

Case II (Fig. 1a)

Box A is now an ideal sinusoidal voltage source. Turning on the alternating voltage (2 to 1) causes the following phenomena. Because of asymmetry of the $I - E$ curve, an alternating voltage about $\bar{E} = 0$ 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 $\bar{E} \neq 0$ 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 $\bar{E}$ 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 $\bar{E} \neq 0$ 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 that¹⁷ the rectification current (I_r) tends to decrease with time. Short circuit of the cell (1 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 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 to 1) produces a current which contains higher harmonic components and also a D.C. component (I_r). There is a

¹⁷A 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.¹⁸ 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

¹⁸Same consideration as in footnote 17.

made here to cover the matter.

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.)¹⁹ 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.²⁰

Discussion of experimental results will be integrated in the

¹⁹G. C. Barker, R. L. Faircloth and A. W. Gardner, Nature, 181, 247 (1958).

²⁰P. Delahay, M. Senda, and C. H. Weis, J. Am. Chem. Soc., in course of publication.

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

¹G. C. Barker, "Faradaic Rectification" in Transactions of the Symposium on Electrode Processes, Philadelphia, 1959, E. Yeager, editor, Wiley, New York, 1960.

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 Vandenbosch² 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-

²V. Vandenbosch, "Contribution a l'étude du dosage polarographique du titane," Bull. Soc. Chim. Belg. 58, 532 (1949).

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_9-t_0 , 5 sec., drop time; t_1-t_0 , 4 sec., age of drop for R.F. pulse; t_5-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 its 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 these delayed pulse generators produces an 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 0.5-50 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 for instance Chance.)³

³Chance et. al., editors, "Waveforms", M.I.T. Radiation Laboratory series Vol. 19, New York, McGraw-Hill Book Co., 1949. Chapt. X. "Time selection."

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 bandwidth limitations, i.e., up to 2 megacycles per second, as the previous stage. This stage had its own power supply.

e) The D.C. Generation Sub-Assembly

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.

f) The Hammer

A low mass 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.

g) The Timing Cams

The timing cams generates the necessary triggering over the long

Fig. 4.-D.C. Generation circuit. R.F. output $4\frac{1}{2}$ 6AS7G in parallel; RY1 hammer: mechanically adapted 5000 ohms relay; RY2 Western Electric mercury relay 276 B; R_K 250 ohms; C_B 0.003 microFarad; R_H 100 ohms Helipot; L_1 , C_1 and L_2 , C_2 General Radio decade inductors 1490-A and General Radio decade capacitors 1419-K; D.C. scope input, Tektronix model E plug-in differential amplifier, R_{L1} and R_{L2} 10 megaohms; R.F. scope input (omitted) between A and ground, Tektronix model G plug-in amplifier, R_{input} 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. μ F.)

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

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

By this method the same value of cell resistance was found for all frequency range used (0.05 - 1MC) 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 wave form 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. wave form 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, criterium 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^{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: $(30.0 \pm 0.1)^\circ\text{C}$

Spontaneous drop time: 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: $2.06 \times 10^{-2} \text{ cm}^2$; and at 1.3 seconds $1.02 \times 10^{-2} \text{ cm}^2$. (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: $(30.0 \pm 0.1)^{\circ}\text{C}$.

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 Weis¹ 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 $|\eta| \ll RT/nF$ can be taken into account by inclusion of the terms in η^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

¹P. Delahay, M. Senda, and C. H. Weis, J. Am. Chem. Soc., in course of publication.

$$\left((nF/RT)|\delta E| \ll 1, |\delta C_0|/C_0^\circ \ll 1, |\delta C_R|/C_R^\circ \ll 1 \right)$$

is written quite generally as

$$\delta I = (\partial I / \partial E) \delta E + (\partial I / \partial C_0) \delta C_0 + (\partial I / \partial C_R) \delta C_R$$

where δ represent a variation of the quantity being considered and the partial derivatives are expressed at the equilibrium potential E_e . This value of δI is identified with that given by eq. (1-4) in which the partial derivatives are computed from eq. (1-3). The variations δC_0 and δC_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 Grahame² 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 δI in terms of δE , δC_0 , and δC_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

²D. C. Grahame, J. Electrochem. Soc., 99, C370 (1952).

curve about E_e . 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 $\delta_p I$

$$\delta_p I = \frac{\partial I}{\partial E} \delta_p E + \frac{\partial I}{\partial C_O} \delta_p C_O + \frac{\partial I}{\partial C_R} \delta_p C_R + \delta_p^2 I \quad (3-1)$$

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

$$\delta_p^2 I = \frac{1}{2} \left\{ \frac{\partial^2 I}{\partial E^2} [(\delta_p E)^2]_p + \frac{\partial^2 I}{\partial C_O^2} [(\delta_p C_O)^2]_p + \frac{\partial^2 I}{\partial C_R^2} [(\delta_p C_R)^2]_p \right\} + \left\{ \frac{\partial^2 I}{\partial E \partial C_O} [\delta_p E \delta_p C_O]_p + \frac{\partial^2 I}{\partial E \partial C_R} [\delta_p E \delta_p C_R]_p + \frac{\partial^2 I}{\partial C_O \partial C_R} [\delta_p C_O \delta_p C_R]_p \right\} \quad (3-2)$$

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

$$\delta_e E = - \frac{\delta_e^2 I}{\partial I / \partial E} \quad (3-3)$$

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 , $\delta_e E$ should be independent of time at least if the double layer capacity is not con-

sidered.

b) General Equation for the Rectification Voltage.

Application of eq. (3-3) requires the derivation of the explicit form of the quantity $\delta_o^2 I$ 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 δ 's must be derived. It is to be noted that the terms in $\partial^2 I / \partial C_0^2$, $\partial^2 I / \partial C_R^2$, and $\partial^2 I / \partial C_0 \partial C_R$ 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 $\Delta \bar{E}_\infty (\equiv \delta_o E)$, is

$$\Delta \bar{E}_\infty = \frac{nF}{RT} V_A \left\{ \frac{2\alpha - 1}{4} + \frac{r_s [(1-\alpha)r_R - \alpha r_0] + y_s [(1-\alpha)y_R - \alpha y_0]}{2(r_s^2 + y_s^2)} \right\} \quad (3-4)$$

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 ($Z = r_F - j y_F$, with $j = (-1)^{1/2}$); and r_0 , r_R , y_0 , 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. We use the symbol $\Delta \bar{E}_\infty$ because $\Delta \bar{E}$ is a function of time when the double layer capacity is considered and the above value corresponds to $t \rightarrow \infty$. One has $r_s = r_{ct} + r_0 + r_R$ (3-6) and $y_s = y_0 + y_R$ (3-7), r_{ct} being the charge transfer resistance per unit area. Values of the r 's and y '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,³ Barker, Faircloth, and Gardner^{4,5,6}, and Vdovin⁷ 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_a^0). They assumed that the current density is $I_a \sin t$ and thus postulated implicitly that the mean current is equal to zero. They wrote the potential as $E_e + \Delta \bar{E}_\infty - V_A \sin (\omega t - \Theta_a)$ 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. (1-3) these values of the current density and E and the values of the concentrations and Θ_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 $\Delta \bar{E}_\infty$.

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

³K.S.G. Doss and H. P. Agarwall, Proc. Indian Acad. Sci., **35A**, 45 (1952).

⁴G. C. Barker, Anal. Chim. Acta, **18**, 118 (1958).

⁵G. C. Barker, R. L. Faircloth, and A. W. Gardner, Nature, **181**, 247 (1958).

⁶G. C. Barker, Transactions of the Symposium on Electrode Processes Philadelphia, May 1959, E. Yeager, editor, Wiley, New York, 1960.

⁷Iu. A. Vdovin, Doklady Akad. Nauk S.S.S.R., **120**, 554 (1958).

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_O and C_R .

The variation of the mean component of the charge q on the electrode thus is $\delta_o q = (dq/dE) \delta_o E$ or $\delta_o q = c_1 \delta_o E$. (3-8 or 9). One also has $\delta_o q = \int_0^t \delta_o I dt$ where $\delta_o I$ 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))

$$\delta_o I = \left[\frac{1}{c_e} \int_0^t \delta_o I dt - \Delta \bar{E}_\infty \right] \frac{\partial I}{\partial E} + \frac{\partial I}{\partial C_O} \delta_o C_O + \frac{\partial I}{\partial C_R} \delta_o C_R \quad (3-10)$$

The changes in concentrations $\delta_o C_O$ and $\delta_o C_R$ can be correlated to the current density as shown by Delahay, Senda, and Weiss, and an equation is obtained which can be solved for $\delta_o I$. Since $\int_0^t \delta_o I dt = c_1 \delta_o E$ the mean rectification voltage $\Delta \bar{E}$ ($\equiv \delta_o E$) is obtained by integration of $\delta_o I$. There follows after substitution of $\partial I / \partial E$, $\partial I / \partial C_O$, and $\partial I / \partial C_R$ by the corresponding values deduced from eq. (1-3).

$$\Delta \bar{E} = \Delta \bar{E}_\infty \left\{ 1 - \frac{1}{c_e} I_a^o \frac{nF}{RT} \frac{1}{G-H} \left[\frac{1}{G} \exp(G^2 t) \operatorname{erfc}(G t^{1/2}) - \frac{1}{H} \exp(H^2 t) \operatorname{erfc}(H t^{1/2}) \right] \right\} \quad (3-11)$$

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

$$G, H = \frac{1}{2} \left\{ \left(\frac{I_a^o}{nF} \right) \left(\frac{1}{C_O^o D_O^{1/2}} + \frac{1}{C_R^o D_R^{1/2}} \right) + \left[\left(\frac{I_a^o}{nF} \right) \left(\frac{1}{C_O^o D_O^{1/2}} + \frac{1}{C_R^o D_R^{1/2}} \right) \right]^2 - 4 I_a^o \frac{nF}{RT} \frac{1}{c_e} \right\}^{1/2} \quad (3-12)$$

One can show from eq. (3-11) that $\Delta \bar{E} = 0$ for $t = 0$ and $\Delta \bar{E} \rightarrow \Delta \bar{E}_\infty$ for $t \rightarrow \infty$. 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 $t \gg 0$ when $c_1 \rightarrow \infty$.

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

$$\Delta \bar{E} = \Delta \bar{E}_\infty \left[1 - \frac{RT}{(nF)^2} \operatorname{erfc} \left(\frac{1}{C_0^0 D_0^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \frac{1}{(\pi t)^{1/2}} \right] \quad (3-13)$$

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 $\Delta \bar{E}_\infty$ is practically reached in a short time (perhaps a few milliseconds) for inherently fast reactions and sufficiently concentrated solutions. The time dependence of $\Delta \bar{E}$ 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. (3-12). Finally, $\Delta \bar{E} / \Delta \bar{E}_\infty$ for a given C_0^0 / C_R^0 also depends on $C_0^0 + C_R^0$ all other conditions remaining constant (Fig. 5).

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. (3-13) 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 pre-supposes no mass transfer polarization for the mean concentrations before variation of the alternating current.

Fig. 5.— Variation of $\Delta \bar{E} / \Delta \bar{E}_{\infty}$ with time according to equation (3-11). Data used in calculations: $D_0 = D_R = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$; $c_1 = 20 \text{ microFarad cm}^{-2}$; $k_a = 1 \text{ cm. sec}^{-1}$; $C_0^{\circ} / C_R^{\circ} = 1$. Numbers on curves refer to value of $n^2(C_0^{\circ} + C_R^{\circ})$.

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_O^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 $[(1/C_O^0 D_O^{1/2}) + (1/C_R^0 D_R^{1/2})]$ 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,⁸ variations of the differential capacity c_1 of the double layer with potential results in a shift of the mean potential

$$\Delta \bar{E}_1 = - \frac{1}{4 c_e} \frac{d c_e}{d E} V_A^2 \quad (3-14)$$

where V_A is the amplitude of the alternating voltage across c_1 . The shift $\Delta \bar{E}_1$ is frequency independent and if $(1/c_1)(dc_1/dE)$ does not

⁸G. C. Barker, Transactions of the Symposium on Electrode Processes, Philadelphia, May 1959, E. Yeager, editor, Wiley, New York, 1960.

Fig. 6.-Tracings of oscillograms of $\Delta\bar{E}$ 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 $\Delta \bar{E}$ 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 $\Delta\bar{E}/\Delta\bar{E}_\infty$ 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 $(1/C_0D_0^{1/2}) + (1/C_RD_R^{1/2})$ in $10^8 \text{ sec}^{1/2} \text{ mol}^{-1} \text{ cm}^2$ for curves 1 to 5: 1.1, 2.8, 4.0, 11.4, 12.0 for $D_0 = D_R = 0.44 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. $\Delta\bar{E}$ and $\Delta\bar{E}_\infty$ were positive for curve 2 and negative for the other curves.

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 $\Delta \bar{E}_1$ of eq. (3-14). The term between brackets in eq. (3-10) now includes $\Delta \bar{E}_1$, and eq. (3-11) is replaced by

$$\Delta \bar{E} = \Delta \bar{E}_\infty - (\Delta \bar{E}_\infty - \Delta \bar{E}_1) \frac{1}{C_2} I_a^\circ \frac{nF}{RT} \frac{1}{G-H} \left[\frac{1}{G} \exp(G^2 t) \operatorname{erfc}(G t^{1/2}) - \frac{1}{H} \exp(H^2 t) \operatorname{erfc}(H t^{1/2}) \right] \quad (3-15)$$

There follows that $\Delta \bar{E} = \Delta \bar{E}_1$ 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 $-\Delta \bar{E}_1$.

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:

$$\Delta \bar{E}_\infty = \frac{nF}{RT} V_A^2 \left\{ \frac{2\alpha-1}{4} - \frac{1}{2} \left[\alpha - \frac{C_O^\circ D_O^{1/2}}{C_O^\circ D_O^{1/2} + C_R^\circ D_R^{1/2}} \frac{1 + \tan \Theta_a}{1 + \tan^2 \Theta_a} \right] \right\} \quad (3-16)$$

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

It follows that $\Delta \bar{E}_\infty = 0$ when $C_O^\circ D_O^{1/2} = C_R^\circ D_R^{1/2}$ and $\alpha = 0.5$, as one would expect. One also infers from eq. (3-16) that $\Delta \bar{E}_\infty$ is proportional to V_A^2 . If the cell resistance is much larger than the

combined impedance of the faradaic impedance in parallel with the double layer capacity, $\Delta \bar{E}_\infty$ 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 H_2 (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 $\Delta \bar{E}_\infty$ 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 $\Delta \bar{E}_\infty$ was examined by Barker⁹ only briefly and in greater detail by Delahay, Senda, and Weis.¹⁰ Two terms in equation (3-16) must be considered, namely V_A and $\cot \Theta_a$. 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 $\omega \rightarrow 0$ and control by kinetics of

⁹G. C. Barker, Transactions of the Symposium on Electrode Processes, Philadelphia, May 1959, E. Yeager, editor, Wiley, New York, 1960.

¹⁰P. Delahay, M. Senda, C. H. Weis, J. Am. Chem. Soc., in course of publication.

Fig. 9.-Variations of $\Delta \bar{E}_\infty$ with the cell R.F. voltage (log-log plot) for 0.7 mM Ti(IV) plus 18.8 mM Ti(III) in 0.88 N 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.

f M.C.	U_A VOLTS	$-\Delta \bar{E}_\infty$ mV.	V_A mV.	$-\Delta \bar{E}_\infty/V_A^2$ VOLTS/VOLTS ²	
				ACTUAL	AVERAGE
.01	.040	.42	15.	1.93	1.79
	.075	1.3	28.	1.65	
.02	.070	.27	13.	1.63	1.72
	.13	1.0	24.	1.75	
	.20	2.4	37.	1.78	
.05	.19	.30	14.	1.52	1.67
	.29	.80	22.	1.74	
	.48	2.3	36.	1.83	
	.90	7.0	67.	1.57	
.1	.36	.28	13.	1.57	1.60
	1.1	2.6	40.	1.58	
	2.3	12.	85.	1.66	
.2	.48	.20	8.8	2.57	1.86
	1.4	1.0	26.	1.51	
	2.2	2.8	40.	1.71	
	3.4	6.4	63.	1.63	
.5	1.2	.14	8.9	1.82	1.59
	2.1	.36	16.	1.50	
	4.0	1.3	30.	1.49	
	6.5	4.0	48.	1.73	
1.	1.6	.05	5.9	1.43	1.77
	3.6	.24	13.	1.35	
	4.8	.8	18.	2.54	

TABLE II

Differential capacity of the supporting electrolyte (0.88 M H_2SO_4 & 0.50 M tartaric acid) for the Ti(IV) / Ti(III) system at 250 cycles per sec.

E Volts vs. S.C.E.	c_1 $\mu\text{Fcm.}^{-2}$
-0.050	31.6
-0.100	30.4
-0.150	29.4
-0.200	28.6
-0.250	28.0
-0.300	27.1
-0.350	26.8
-0.400	25.5
-0.450	24.5
-0.500	23.4
-0.550	22.4
-0.600	21.6
-0.650	-
-0.700	20.6

TABLE III

Data for $\Delta \bar{E}_\infty$ for the discharge of 1mM Hg_2^{++} in 1.14 M HClO_4 for two electrode areas

DROP AGE	1.30 sec.			3.70 sec.		
DROP AREA	$1.02 \times 10^{-2} \text{ cm}^2$			$2.06 \times 10^{-2} \text{ cm}^2$		
f	U_A	$-\Delta \bar{E}_\infty$	$-\Delta \bar{E}_\infty / I_A^2$	U_A	$-\Delta \bar{E}_\infty$	$-\Delta \bar{E}_\infty / I_A^2$
MC.	VOLTS	mV.	$10^{-3} \text{ V.} \left(\frac{\text{AMP.}}{\text{cm}^2} \right)^{-2}$	VOLTS	mV.	$10^{-3} \text{ V.} \left(\frac{\text{AMP.}}{\text{cm}^2} \right)^{-2}$
0.15	.065	.050	3.6	.125	.050	4.0
	.10	.125		.25	.22	
	.145	.30		.32	.38	
0.30	.11	.050	1.4	.21	.050	1.5
	.19	.175		.38	.175	
	.24	.30		.48	.32	
0.60	.17	.050	0.48	.34	.050	0.49
	.32	.175		.50	.10	
	.44	.30		.95	.38	
1.00	.40	.100	0.18	.65	.050	0.18
	.54	.20		.90	.125	
	.80	.40		1.6	.43	
1.50	.75	.15	0.076	1.3	.11	0.077
	1.15	.35		1.6	.15	

charge transfer for $\omega \rightarrow \infty$. One has $\text{ctn } \Theta_a \rightarrow 1$ for diffusion control and

$$\left(\frac{\Delta \bar{E}_\infty}{V_A^2} \right)_{\omega \rightarrow 0} = \frac{nF}{4RT} \frac{C_O^0 D_O^{1/2} - C_R^0 D_R^{1/2}}{C_O^0 D_O^{1/2} + C_R^0 D_R^{1/2}} \quad (3-17)$$

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, $\Delta \bar{E}_\infty / I_A^2$ 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,

$$\left(\frac{\Delta \bar{E}_\infty}{V_A^2} \right)_{\omega \rightarrow \infty} = \frac{nF}{4RT} (2\alpha - 1) \quad (3-18)$$

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

$$\frac{1}{\text{ctn } \Theta_a} = \frac{I_a^0}{2^{1/2} nF} \left(\frac{1}{C_O^0 D_O^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \frac{1}{\omega^{1/2}} \quad (3-19)$$

provided that $\omega^{1/2} \gg 10^3 \text{ k}_a^0$; ($D_O = D_R = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, $C_O^0 = C_R^0$).

Under these conditions, $\Delta \bar{E}_\infty / V_A^2$ varies linearly with $1/\omega^{1/2}$.

The transfer coefficient α 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, α can also be determined from the variations of I_a^0 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

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

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^{+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^{+2} gave the limiting value $\Delta \bar{E}_\infty / V_A^2 = 20 \pm 5 \text{ volt}^{-1}$ for an assumed differential capacity of 160 microfarad. cm^{-2} . This is the limiting value $nF/4RT$ for $n = 2$ in this case. No accurate verification was possible because the double layer capacity cannot be measured in this case.

c) Variations of $\Delta \bar{E}_\infty / V_A^2$ with the Ratio C_O^0 / C_R^0 .

Variations of $\Delta \bar{E}_\infty / V_A^2$ with the ratio C_O^0 / C_R^0 , i.e., with the equilibrium potential, were also examined. This analysis is directly

Fig. 10.-Plot of $\log(\Delta \bar{E}_\infty / I_A^2)$ versus $\log \omega$ for the discharge of Hg_2^{++} at different concentrations (mM per liter) in 1.14 M perchloric acid. $\Delta \bar{E}_\infty$ was negative for all concentrations

Fig. 11.--Plot of $(4RT/nF)(\Delta \bar{E}_\infty/V_A^2)$ against $(nF/RT)(E_e - E_{1/2})$ for different values of $k_a^0/(2\omega D)$, D being the common value of D_O and D_R . $\alpha = 0.25$. Values of $k_a^0/(2\omega D)$ for curves 1 to 9: $\infty, 1, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, \text{zero}$.

derived from that of Barker¹¹ who considered $\Delta \bar{E}_\infty$ (which vanishes for $\omega \rightarrow \infty$) rather than $\Delta \bar{E}_\infty / V_A^2$. Two limiting cases will be considered: $\omega \rightarrow 0$ and $\omega \rightarrow \infty$ for which eqs. (3-17) and (3-18) apply, respectively.

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

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

This quantity approaches ± 1 for $E_e \rightarrow \pm \infty$ and is equal to zero for $E_e = E_{1/2}$. Hence $\Delta \bar{E}_\infty / V_A^2 = \pm nF/4RT$ for $E_e \rightarrow \pm \infty$ and $\omega \rightarrow 0$. equation (3-17) applies for $\omega \rightarrow \infty$, and $\Delta \bar{E}_\infty / V_A^2 \gtrless 0$ for $\alpha \gtrless 0.5$. 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

$$\tanh \left[\frac{1}{2} \frac{nF}{RT} (E_e - E_{1/2}) \right] = (2\alpha - 1) \quad (3-21)$$

The parameter α 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 $\alpha = 0.25$ and $\alpha = 0.46$ 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:

¹¹The same as note 9 in this chapter.

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

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 $\Delta \bar{E}_\infty$ is measured: t must be long enough to allow $\Delta \bar{E}_\infty$ 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^0 's could be increased.

Attainment of $\Delta \bar{E}_\infty$ 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 per cent for $t > 5 r c$, r being the total resistance of the circuit connected to the alternating current generator and c , for control of $\bar{I} = 0$, 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 $\Delta \bar{E}_\infty$. Since $|\Delta \bar{E}_\infty| < (nF/4RT)V_A^2$ and $V_A \leq 0.005$ volts, one has $|\Delta \bar{E}_\infty| \approx 100n$ to $200n$ microvolts. Further $|dE_e / dt| \leq 1$ millivolt. degree⁻¹ 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 $dT/dt = 0.24 (I_A^2/2) (1/\kappa_e \delta_e C_h)$ at the electrode surface, κ_e being the specific conductance of the electrolyte, C_h its specific heat, and δ_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.), $dT/dt = 0.3$ degrees. sec.⁻¹. Since one should have $\Delta T < 0.001$ to 0.01 degree, $\Delta \bar{E}_\infty$ 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 $\Delta \bar{E}_\infty$ by means of a low pass filter. Requirements for this filter become more stringent as the resistance increases as one can readily show. Let $\underline{U}$ (Fig. 13) represent the total voltage composed of a low frequency component $\underline{E}$ (including D.C.) and a high frequency component $\underline{V}_L$. "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

$$E_{out} = E_{in} \quad (3-22)$$

and

$$V_{out} = \left(\frac{\omega_0}{\omega} \right)^m V_{in} \quad (3-23)$$

for $\omega \gg \omega_0$, ω_0 being the cut-off frequency. For a simple L-C low pass filter $m = 2$. The faradaic rectification voltage can be written as

$$E_{in} = k_R \frac{1}{R_c \omega^2} V_{in}^2 \quad (3-24)$$

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

$$\frac{E_{out}}{V_{out}} \gg 1 \quad (3-25)$$

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

$$\frac{E_{out}}{V_{out}} = k_R \frac{\omega^{(m-2)}}{R_c^2 \omega_0^m} V_{in} \quad (3-26)$$

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_O^0 / C_R^0 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 O 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 White¹² 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_O^0 / C_R^0 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 $\bar{I} = 0$.

¹²J. E.B. Randles and W. White, Z. Elektrochem. 59, 666 (1955).

CHAPTER IV

CONCLUSIONS

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 Delahay¹ 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 α 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 α even when the cell resistance is very much larger than the charge transfer resistance.

¹P. Delahay, "The Study of Fast Electrode Reactions by Relaxation Methods", Chapter 5 in "Advances in Electrochemistry and Electrochemical Engineering". P. Delahay and C. W. Tobias, editors, Interscience Publishing Co., New York, in course of publication.

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 ($D = 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1}$) for $t = 10^{-8} \text{ sec.}$ 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 Laboratory 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.

A P P E N D I X

As noted in Chapter III equation (3-4) is deduced from equation (3-3) in which $\delta_0^2 I$ is derived from equation (3-2). Further the terms in $\partial^2 I / \partial C_R^2$, $\partial^2 I / \partial C_O^2$, and $\partial^2 I / \partial C_R \partial C_O$ 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 O and R (cf. eq. 1-3). The problem thus is to express $\delta_1 C_O$ and $\delta_1 C_R$ 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)

$$\delta_1 I = - \frac{\delta_1 E}{r_s - j y_s} \quad (A-1)$$

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 O and R (diffusion, homogeneous or heterogeneous chemical reaction, etc.) are independent of potential, one has for species i ($\equiv$ O or R)

$$\delta_1 C_i = \mp \left[(h_x)_i - j (h_y)_i \right] \delta_1 I \quad (A-2)$$

where the sign hold for O and R respectively, and h_x 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 $\delta_i C_i$ from equation (A-2) into

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

one obtains after re-arrangement of terms

$$\delta_i I = \frac{-\delta_i E}{-\frac{1}{\frac{\partial I}{\partial E}} + \frac{\frac{\partial I}{\partial C_R} (h_R)}{\frac{\partial I}{\partial E}} - \frac{\frac{\partial I}{\partial C_O} (h_O)}{\frac{\partial I}{\partial E}} - \gamma \left[\frac{\frac{\partial I}{\partial C_R} (h_Y)}{\frac{\partial I}{\partial E}} - \frac{\frac{\partial I}{\partial C_O} (h_Y)}{\frac{\partial I}{\partial E}} \right]} \quad (A-4)$$

or

$$\delta_i I = \frac{-\delta_i E}{n_{ct} + n_R + n_O - \gamma (y_R + y_O)} \quad (A-5)$$

where r_{ct} , r_R , r_O , y_R , y_O 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 ($i \equiv O$ or R)

$$\delta_i C_i = \left[(\partial I / \partial E) / (\partial I / \partial C_i) \right] (n_i - \gamma y_i) \delta_i I \quad (A-6)$$

or after combination with equation (A-1)

$$\delta_i C_i = - \left[(\partial I / \partial E) / (\partial I / \partial C_i) \right] \left(\frac{n_i - \gamma y_i}{n_s - \gamma y_s} \right) \delta_i E \quad (A-7)$$

A general equation for $\delta_o^2 I$ 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 :

$$\partial I / \partial E = - I_a^0 (nF/RT) ,$$

$$\partial I / \partial C_O = I_a^0 / C_O^0 ,$$

$$\partial I / \partial C_R = - I_a^0 / C_R^0 ,$$

$$\partial^2 I / \partial E^2 = - I_a^0 [(1-\alpha)^2 - \alpha^2] ,$$

$$\partial^2 I / \partial E \partial C_O = - (I_a^0 / C_O^0) (\alpha nF/RT) ,$$

$$\partial^2 I / \partial E \partial C_R = - (I_a^0 / C_R^0) [(1-\alpha) nF/RT] ,$$

$$-(\partial I / \partial E) / (\partial I / \partial C_O) = (nF/RT) C_O^0 ,$$

and finally

$$-(\partial I / \partial E) / (\partial I / \partial C_R) = -(nF/RT) C_O^0 .$$

SELECTED BIBLIOGRAPHY

- Barker, G. C. "Square Wave Polarography and some Related Techniques", Anal. Chim. Acta, **18**, 118 (1958).
- Barker, G. C., R. L. Faircloth and A. W. Gardner "Use of Faradaic Rectification for the Study of Rapid Electrode Processes", Nature, **181**, 247 (1958).
- Barker, G. C. "Faradaic Rectification", in Transactions of the Symposium on Electrode Processes, Philadelphia, 1959, E. Yeager, editor, New York, Wiley, 1960.
- Chance, B. et. al., editors, "Waveforms", M.I.T. Radiation Laboratory Series Vol. 19, New York, McGraw-Hill Book Co., 1949. Chapt. X. "Time Selection".
- Delahay, P. "The Study of Fast Electrode Reactions by Relaxation Methods", Chapter 5 in "Advances in Electrochemistry and Electrochemical Engineering", P. Delahay and C. W. Tobias, editors, New York, Interscience Publishing Co., in course of publication.
- Delahay, P., M. Senda, and C. H. Weis "Faradaic Rectification and Electrode Processes", J. Am. Chem. Soc., in course of publication.
- Doss, K.S.G. and H. P. Agarwall "A New Polarization Effect: Redoxokinetic Potential", J. Sci. Industr. Res. India **9B**, 280 (1950).
- Doss, K.S.G. and H. P. Agarwall "The Theory of the Redoxokinetic Effect and a General Method for the Determination of α of Absolute Reaction Rates," Proc. Indian Acad. Sci., **34A**, 263 (1951).
- Doss, K.S.G. and H. P. Agarwall "The Theory of Redoxo-Kinetic Effect: A Correction," Proc. Indian Acad. Sci., **35A**, 45 (1952).
- Fournier, M. "Influence de la fréquence de la tension appliquée à une électrode à goutte de mercure. Étude des courbes polarographiques", Compt. rend. Acad. Sci. Paris, **232**, 1673 (1951).
- Grahame, D. C. "Mathematical Theory of the Faradaic Admittance (Pseudocapacity and Polarization Resistance)", J. Electrochem. Soc., **99**, C370 (1952).
- Matsuda, H. and P. Delahay "Faradaic Rectification with Control of Alternating Potential Variations", J. Am. Chem. Soc., **82**, 1547 (1960).

- Oldham, K. B. "Faradaic Rectification: Theory and Applications to the Hg_2^2/Hg Electrode," Trans. Faraday Soc. 53, 80 (1957).
- Randles, J.E.B. and W. White "Reactions of Metal Ions at Mercury Electrodes in Fused Salts," Z. Elektrochem. 59, 666 (1955).
- Senda, M. and I. Tachi "Studies on A.C. Polarography. V. Theory of Reversible Wave," Bull. Chem. Soc. Japan, 28, 632 (1955).
- Vandenbosch, V. "Contribution à l'étude du dosage polarographique du titane," Bull. Soc. Chim. Belg. 58, 532 (1949).
- Vdovin, Iu. A. "The Theory of the Faradaic Rectification," Doklady Akad. Nauk S.S.S.R., 120, 554 (1958).

VITA

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EXAMINATION AND THESIS REPORT

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Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

July 26, 1960