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Electrode Kinetics at Open Circuit at the Streaming Mercury Electrode.

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AT THE STREAMING MERCURY ELECTRODE.

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ELECTRODE KINETICS AT OPEN CIRCUIT
AT THE STREAMING MERCURY ELECTRODE

A Dissertation

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requirements for the degree of
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in

The Department of Chemistry

by
Vakula S. Srinivasan
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ABSTRACT

The algebraic sum of the faradaic and double layer charging currents is equal to zero for an electrode of varying area at open circuit. There results a shift of the open circuit potential, and this shift can be correlated to the kinetic parameters for the electrode process. Detailed analysis of this phenomenon has been carried out in this laboratory. Cases of mixed control by mass transfer and charge transfer, control by mass transfer and control by charge transfer were studied with the streaming mercury electrode.

The following systems were studied: (a) discharge of Hg(I) in 1 M perchloric acid as example of mass transfer controlled process; (b) the Cr(III)/Cr(II) couple in 1 M potassium chloride as a charge transfer controlled process; (c) the V(III)/V(II) in 1 M perchloric acid and the Zn(II)/Zn(Hg) in 1 M potassium chloride and 1 M potassium thiocyanate as processes with mixed control by mass transfer and charge transfer.

The charging current of the streaming mercury electrode was also investigated, and observations were made on the discharge of Hg(I) and Hg(II) with mixed control by diffusion and migration.

CHAPTER I

INTRODUCTION

When a quantity of electricity passes across an electrolyte-metal or a molten salt-metal interface two processes must be considered: (1) the non-faradaic charging of the electrical double layer; and (2) the faradaic charge transfer process corresponding to an electrode reaction, i.e., a process involving net oxidation or reduction. These two processes will be briefly reviewed.

1) The Electrical Double Layer

Electrolyte-metal interfaces behave like an electric capacitor but, unlike an electric capacitor, the capacitance of the interface depends upon the electrode potential, as measured against some reference electrodes, and the composition of the solution. Hence the study of the capacity of the interface throws light on the properties of the interface. (See Grahame's review¹ and Delahay's monograph.²)

¹D. C. Grahame, "The Electrical Double Layer and the Theory of Electrocapillarity", Chem. Rev., 41, 441 (1947).

²P. Delahay, "Double Layer and Electrode Kinetics", Interscience-Wiley, New York, in press.

We consider an ideal polarized mercury electrode in equilibrium with the electrolyte, that is, an electrode in the absence of any electrode reactions. It is evident that the algebraic sum of the charges on either side of the interface is equal to zero. If the charge on the metal side is positive, anions are predominant in the immediate vicinity of the interface, in the solution side and vice versa. Thus a clear charge separation at the interface gives rise to the electrical capacitance-like behavior.

A thermodynamic approach to correlate the experimentally observed surface properties and the composition of the solution has been made by G. Lippmann as early as 1875. In his famous equation, which is derivable from Gibbs' adsorption isotherm, the surface tension is related to the charge at the interface and the composition of the solution. Thus, one has at constant temperature and pressure and for a solution of a single electrolyte

$$-d\gamma = q_m dE_{\pm} + \bar{\Gamma}_{\mp} d\mu \quad (1-1)$$

is the interfacial tension, q_m the charge on the electrode, $E_{\pm}$ the potential with respect to a reference electrode which is reversible to the cation or the anion, respectively, $\bar{\Gamma}_{\mp}$ is the anion ($\bar{\Gamma}_{-}$) or the cation

(Γ_+) relative surface excess, and μ is the electrolyte chemical potential. It follows from the above equation that the charge on the electrode per unit area is given by

$$q_n = - \left(\frac{\partial \gamma}{\partial E} \right) \mu \quad (1-2)$$

at constant temperature and pressure, the chemical potentials μ being kept constant. Equation 1-1 can be generalized for mixtures of several electrolytes.

Thus, the charge on the electrode is a thermodynamic quantity which can be determined from the variations of surface tension with E the potential (electrocapillary curve). The γ versus E curve has the shape of a parabola but is not a parabola. The potential for which $\left(\frac{\partial \gamma}{\partial E} \right) = 0$ is the point of zero charge or E_z , which is also referred to as electrocapillary maximum (E.C.M.). It is sometimes convenient to express the potential of the electrode with respect to the point of zero charge, and potentials in this scale as referred to as "rational potentials". The sign of the charge on the electrode is that of the rational potential.

The interface capacity can be defined in two ways: (1) by the integral capacity c_1 according to

$$q_m = c_1 (E - E_z) \quad (1-3)$$

or (2) by the differential capacity c_d according to

$$c_d = \left(\frac{dq_m}{dE} \right)_{p,T,\mu} \quad (1-4)$$

One has

$$q_m = \int_{E_z}^E c_d dE \quad (1-5)$$

2) Faradaic Charge-Transfer Processes

We consider a simple electrode reaction with a single rate determining step corresponding to the equation

where both the components are soluble in the electrolyte and/or electrode. In the absence of complications due to mass transfer or a coupled chemical reaction, the current density-potential variations for reaction 1-6 are accounted for by the equation

$$I = I_a^0 \left[\exp\left(-\frac{\alpha nF}{RT} \eta\right) - \exp\left(\frac{(1-\alpha) nF}{RT} \eta\right) \right] \quad (1-7)$$

where I_a^0 , the apparent exchange current density and α , the transfer coefficient, are the parameters characterizing the reaction kinetics. The overvoltage η is equal to $(E - E_e)$, 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. Equation 1 - 7 is

written for the convention according to which a net reduction (cathodic) current is positive and net oxidation (anodic) current is negative.

If the concentrations of O and R at the electrode surface C_O and C_R are different from the concentrations in the bulk of the solution C_O^0 and C_R^0 , mass transfer polarisation should be considered. Then equation 1-7 becomes

$$I = I_a^0 \left\{ \frac{C_O}{C_O^0} \exp\left[-\frac{\alpha n F}{RT} \eta\right] - \frac{C_R}{C_R^0} \exp\left[(1-\alpha) \frac{n F}{RT} \eta\right] \right\} \quad (1-8)$$

3) Combination of Double Layer Charging with Faradaic Charge Transfer

A simple way of representing both the transfer processes is given Fig. 1 from which it is seen that the charge-transfer process corresponds in effect to "leakage" of the double layer capacity.

The presence of a non-faradaic process limits the sensitivity of most existing electro-analytical techniques based on measurement of a faradaic current. However, in the recently developed coulometric method^{3,4} the potential of the electrode is changed in a very short time (microsecond-duration) and the subsequent variations

³p. Delahay, "Fundamentals of Coulometric Analysis", Anal. Chem., 34, 1267 (1962).

⁴p. Delahay, "Coulometric Method for the Kinetic Study of Fast Electrode Processes. I. Theory", J. Phys. Chem., 66, 2204 (1962).

Fig. 1 - Equivalent circuit of the electrode-solution interface, during an electrode process. R_s is the solution resistance, C_{dl} the double-layer capacity and Z_F is the element corresponding to the faradaic charge-transfer process.

of potential are followed. A logical extension of the same concept leads to the principle of the work reported here. Instead of using an external source of electrical energy, the electrode reaction itself is used to provide the charge for the double layer, and consequently the study of potential shift from the equilibrium value provides information regarding the kinetic parameters.

4) Previous Work

It was observed by J. E. Rosenberg and G. Stegeman⁵ that a jet of streaming mercury electrode develops a potential different from that of a stationary mercury pool in a solution of mercury ions. Though their general observations were correct, they wrongly attributed this effect to the difference in the rates of adsorption of mercury ions on the stationary electrode and the streaming mercury electrode. Schofield⁶ in his study of expanding mercury electrodes concluded that "on increasing the area of either a flux of electricity must pass across the interface or an equivalent amount of mercurous sulphate must diffuse up to it from the solution (or be produced there by a chemical action) in order to bring equilibrium between the phases."

⁵J. E. Rosenberg and G. Stegeman, "The Adsorption of Ions by Metallic Mercury", J. Phys. Chem., 30, 1306 (1926).

⁶R. K. Schofield, "Verification of Gibbs' Adsorption Equation", Phil. Mag., (7) 1, 641 (1926).

This author arrived at this conclusion while doing experiments to verify Gibbs' adsorption equation.

Watanabe and his coworkers (see review in ref. 7) used a vibrating mercury electrode to measure double layer capacity but they did not consider the possibility of studying electrode kinetics.

Spear⁸ studied the variations of potential of a mercury electrode of varying area as resulted from the flow of mercury from a funnel of suitable profile. He considered the ideal polarized electrode (no faradaic process) and the case of oxygen reduction. The idea of compensation of the charging current by this faradaic current was clearly stated by Spear. The same idea was independently stated by Delahay⁹ and applied to the streaming mercury electrode.

5) Purpose of This Work

The aim of this work is to show how the potential of an electrode of varying area can be explained on the basis of compensation of the double layer charging

⁷A. Watanabe, "A. C. Methods in Interfacial Electrical Phenomenon", J. Electrochem. Soc., 110, 72 (1963).

⁸C. D. Spear, "Transient Electrode Potentials of Mercury", dissertation, University of Utah, 1960; microfilms Inc., Ann Arbor, Michigan.

⁹P. Delahay "Electrode Kinetics at Open Circuit at the Streaming Mercury Electrode. I. Theory", J. Electroanal. Chem., in press.

current by a faradaic current. The study will be made in the particular case of the streaming mercury electrode. The following cases are examined: pure mass-transfer control, pure charge transfer control, and mixed control by charge transfer and mass transfer.

CHAPTER II

THEORETICAL ANALYSIS OF THE POTENTIAL OF THE STREAMING MERCURY ELECTRODE

The following analysis, according to Delahay¹, is necessary for the intelligent discussion of experimental results in subsequent chapters.

Consider an electrode which exhibits the equilibrium potential E_e corresponding to the charge transfer reaction,

assuming both O and R are soluble, for given activities of O and R. If the area A of electrolyte-electrode interface varies, the double layer capacity which is proportional to area varies. There results a double layer charging current or capacity current which, at open circuit, must be entirely compensated by some faradaic current. If we assume that the above reaction only occurs at the electrode, this reaction proceeds with an overvoltage η , which can be measured with an instrument of high input impedance. Hence the current potential characteristics can be determined at open circuit by varying the capacity current density, i. e. by changing $\left(\frac{1}{A}\right)\left(\frac{dA}{dt}\right)$, where t is the time.

¹p. Delahay "Electrode Kinetics at Open Circuit at the Streaming Mercury Electrode. I. Theory", J. Electroanal. Chem., in press.

1) General Equation

The charge q_m on the electrode can be written as

$$q_m = c(E-E_z)A \quad (2-2)$$

where c is the integral capacity of the double layer expressed for a unit area (heretofore written as c_1), E the potential of the electrode expressed according to the Stockholm I.U.P.A.C. convention, and E_z the point of zero charge. If the charge on the electrode varies as the area varies with time by differentiating equation 2-2 with respect to time one gets the capacity current at any instant as

$$i_c = \frac{dq}{dt} = (E-E_z) A \left(\frac{dc}{dE} \right) \left(\frac{dE}{dt} \right) + c A \left(\frac{dE}{dt} \right) + c (E-E_z) \frac{dA}{dt} \quad (2-3)$$

If this quantity is positive, a positive charge must be supplied to the electrode, and a net cathodic reaction should occur at the electrode at open circuit. Conversely, a net anodic reaction occurs at open circuit when the above quantity is negative. In general, the term in $\left(\frac{dc}{dE} \right)$ is small or negligible and it can be assumed in the analysis of various electrodes that c is independent of E in the interval of potential considered. If furthermore conditions are such that

$$\left| c A \left(\frac{dA}{dt} \right) \right| < \left| c (E-E_z) \frac{dA}{dt} \right| \quad (2-4)$$

the net reaction is cathodic or anodic, respectively, according to $c(E-E_z)(\frac{dA}{dt}) \gtrless 0$.

Since we adopted, in chapter I, for the faradaic current density I_f the common convention that $I_f \gtrless 0$ for cathodic or anodic process respectively, we write at open circuit

$$(E-E_z)A\left(\frac{dc}{dE}\right)\left(\frac{dE}{dt}\right) + cA\left(\frac{dE}{dt}\right) + c(E-E_z)\left(\frac{dA}{dt}\right) \cdot I_f \quad (2-5)$$

This equation is valid for any type of electrode.

2) The Case of the Streaming Mercury Electrode

In the study that follows, a streaming mercury electrode of the Heyrovsky² type characterized by a length l and a rate of flow of mercury m is used. The radius r of the mercury column in contact with the solution is assumed to be constant. There is a continual removal of a film of solution with the mercury jet. There results a charging current although the electrode area exposed to the solution is constant.

²J. Heyrovsky and Forjet, "Oszillographische Polarographie", Z. Physik. Chem., 193, 83 (1943).

a) Capacity Current

If we consider an elemental area on the streaming electrode, we have

$$\begin{aligned} \text{capacity current} &= \\ c(E-E_z) \times \text{rate of removal of mercury} &\quad (2-6) \end{aligned}$$

$$\begin{aligned} \text{Rate of removal} &= \\ \frac{\text{Area}}{\text{Time to travel the length of the column}} &\quad (2-7) \end{aligned}$$

$$\text{Area} = 2 \pi r l \quad (2-8)$$

$$\text{Time} = \frac{\text{Length of the jet}}{\text{Velocity of the jet}} = \frac{l}{v} \quad (2-9)$$

but the velocity

$$v = \frac{m}{\pi r^2 \delta} \quad (2-10)$$

where δ is the density of mercury. Hence,

$$\text{rate of removal of mercury} = \frac{2m}{r\delta} \quad (2-11)$$

and the capacity current is given as

$$i_c = c(E-E_z) \frac{2m}{r\delta} \quad (2-12)$$

Equation 2-12 shows that the capacity current is independent of the length of the jet and depends only on the mass flow rate and the radius of the jet.

b) Faradaic Current

From equation 1-8 it is possible to write for the faradaic current density

$$I_f = I_a^0 \left[\left(1 - \frac{I_f}{I_c^d}\right) \exp\left[-\frac{\alpha n F \eta}{RT}\right] - \left(1 + \frac{I_f}{I_a^d}\right) \exp\left[\frac{(1-\alpha) n F \eta}{RT}\right] \right] \quad (2-13)$$

if we substitute for

$$\frac{C_o}{C_o^0} = 1 - \frac{I_f}{I_c^d} \quad \text{and} \quad \frac{C_a}{C_a^0} = 1 + \frac{I_f}{I_a^d} \quad (2-14)$$

from Nernst diffusion model. I_c^d and I_a^d are the cathodic and anodic diffusion current densities respectively.

Rearrangement of this equation gives,

$$I_f = \frac{\exp\left[-\frac{\alpha n F \eta}{RT}\right] - \exp\left[\frac{(1-\alpha) n F \eta}{RT}\right]}{\frac{1}{I_c^d} + \frac{\exp\left[-\frac{\alpha n F \eta}{RT}\right]}{I_c^d} + \frac{\exp\left[\frac{(1-\alpha) n F \eta}{RT}\right]}{I_a^d}} \quad (2-15)$$

The meanings of the notations used are already explained in the introduction. It is reminded, however, that one has $I_f \geq 0$ for $\eta \leq 0$.

c) The General Case

The current densities I_c^d and I_a^d vary along the length of the mercury column. The case of mass transfer by diffusion at the streaming mercury electrode has been treated by Koryta³ making the following assumptions:

³J. Koryta, "Diffusion and Kinetic Currents at the Streaming Mercury Electrode", Coll. Czechoslov. Chem. Commun., 19, 433 (1954).

1) The layer of solution in the immediate vicinity of the electrode is set in motion by the streaming mercury so that it moves at the same speed as mercury.

2) The moving layer is thicker than the diffusion layer.

3) The concentration gradient in the moving layer is perpendicular to the electrode surface. The concentration gradient parallel to the electrode surface is negligible.

4) The diffusion layer is very thin and semi-infinite linear diffusion is the sole mode of mass transfer.

Koryta obtained for the total current,

$$i_d = 4 \pi F \sqrt{\frac{D l m}{\rho}} C^{\circ} \quad (2-16)$$

The current density I^d is

$$I^d = \frac{\pi F D^{1/2} C^{\circ}}{\pi r \rho^{1/2}} \left(\frac{m}{l}\right)^{1/2} \quad (2-17)$$

m denotes the rate of flow of mercury in gm. sec^{-1} and l the length of the mercury jet in cm. D expressed in $\text{cm}^2 \cdot \text{sec}^{-1}$ is the diffusion coefficient of the substance being reduced or oxidized at the electrode. ρ is the density of mercury flowing.

It can be seen from equations 2-16 and 2-17 that the faradaic current is directly proportional to $l^{1/2}$ and the faradaic current density is inversely proportional to $l^{1/2}$.

Considering an element of length dl of the mercury jet, from equations 2-15 and 2-17 one can write for faradaic current

$$di_f = I_f^0 2\pi r dl$$

$$di_f = \frac{2\pi r \left[\exp\left[-\frac{\alpha n F \eta}{RT}\right] - \exp\left[\frac{(1-\alpha) n F \eta}{RT}\right] \right] dl}{\frac{1}{I_a^0} + \frac{\pi r^2}{n F} \left[\frac{\exp\left[-\frac{\alpha n F \eta}{RT}\right]}{C_o^0 D_o^{1/2}} - \frac{\exp\left[\frac{(1-\alpha) n F \eta}{RT}\right]}{C_R^0 D_R^{1/2}} \right] \left(\frac{l}{m}\right)^{1/2}} \quad (2-18)$$

writing

$$S = 2\pi r \left[\exp\left[-\frac{\alpha n F \eta}{RT}\right] - \exp\left[\frac{(1-\alpha) n F \eta}{RT}\right] \right] \quad (2-19)$$

and

$$N = \frac{\pi r^2}{n F} \left[\frac{\exp\left[-\frac{\alpha n F \eta}{RT}\right]}{C_o^0 D_o^{1/2}} + \frac{\exp\left[\frac{(1-\alpha) n F \eta}{RT}\right]}{C_R^0 D_R^{1/2}} \right] \quad (2-20)$$

one writes

$$di_f = \frac{S dl}{\frac{1}{I_a^0} + N \left(\frac{l}{m}\right)^{1/2}} \quad (2-21)$$

integrating this equation over the limits $l = 0$ from the orifice of the capillary to $l = l$, the point at which the solution breaks we get (see appendix 1)

$$i_f = \frac{2Sm}{N^2} \frac{1}{I_a^0} \left[\lambda - \ln(1+\lambda) \right] \quad (2-22)$$

where

$$\lambda = N I_a^0 \left(\frac{l}{m}\right)^{1/2}$$

When steady state is reached, equation 2-12 for the capacity current can be equated to equation 2-22 for faradaic current. Thus

$$\frac{2m}{r\delta} c (E-E_2) = \frac{2Sm}{N^2} \frac{1}{I_a} [\lambda - \ln(1+\lambda)] \quad (2-23)$$

from which one gets (see appendix 2)

$$G(\eta) = \frac{2nFr\delta^{1/2}}{c} \left(\frac{l}{m}\right)^{1/2} \left[1 - \frac{1}{\lambda} \ln(1+\lambda)\right] \quad (2-24)$$

with

$$G(\eta) = (E-E_2) \cdot \frac{\frac{1}{C_o^{1/2} D_o^{1/2}} + \frac{\exp(\frac{nF}{RT}\eta)}{C_R^{1/2} D_R^{1/2}}}{(1 - \exp(\frac{nF}{RT}\eta))} \quad (2-25)$$

and

$$\lambda = \frac{\pi r\delta^{1/2}}{nF} \left\{ \frac{\exp[-\frac{nF}{RT}\eta]}{C_o^{1/2} D_o^{1/2}} + \frac{\exp[\frac{(1-\alpha)nF}{RT}\eta]}{C_R^{1/2} D_R^{1/2}} \right\} \quad (2-26)$$

here c is taken at the potential E corresponding to the particular value of (l/m) at which the electrode operates. It is seen that $G(\eta)$ is proportional to $(l/m)^{1/2}$ and to the function $\left[1 - \frac{1}{\lambda} \ln(1+\lambda)\right]$.

It is possible to write

$$\begin{aligned} (E-E_2) &= (E-E_e) + (E_e-E_2) \\ &= \eta + (E_e-E_2). \end{aligned} \quad (2-27)$$

hence $G(\eta)$ is an experimental quantity. For each point corresponding to a particular $(l/m)^{1/2}$ one can calculate the value for the argument in the equation 2-24. A plot relating $1 - \frac{1}{\lambda} \ln(1+\lambda)$ is made (Fig. 2) from which the corresponding for the calculated argument can be found.

Fig. 2 - Plot for finding λ from the experimentally determined argument.

Taking the logarithms of both sides of equation 2-26 and rearranging one can write,

$$\ln \lambda \cdot \frac{nF}{\pi r^2 \delta^{1/2}} \cdot \frac{1}{\frac{1}{C_0 D_0^{1/2}} + \frac{\exp[\frac{nF\eta}{RT}]}{C_R D_R^{1/2}}} \cdot \left(\frac{l}{m}\right)^{1/2} = \ln I_a^0 - \frac{\alpha nF}{RT} \eta \quad (2-28)$$

Hence a plot of experimentally determined quantity on the left handside of equation 2-28 versus η gives the values of α from the slope and I_a^0 from the intercept.

d) Mass Transfer Controlled Process

For a diffusion controlled process I_a^0 is very high and so $\lambda \rightarrow \infty$. Then argument $1 - \frac{1}{\lambda} \ln(1+\lambda) \rightarrow 1$. Instead of 2-24 we get

$$G(\eta) = \frac{2nF\tau\delta^{1/2}}{C} \left(\frac{l}{m}\right)^{1/2} \quad (2-29)$$

e) Charge Transfer Controlled Process

For a charge transfer controlled process $D \rightarrow \infty$, so $\lambda \rightarrow 0$. Then $1 - \frac{1}{\lambda} \ln(1+\lambda)$ tends towards $\frac{\lambda}{2}$. After proper substitution equation 2-24 reduces to,

$$\frac{E - E_2}{\exp\left[-\frac{\alpha nF}{RT} \eta\right] - \exp\left[\frac{(1-\alpha)nF}{RT} \eta\right]} = \frac{\pi r^2 \delta}{C} I_a^0 \left(\frac{l}{m}\right) \quad (2-30)$$

f) Small Overvoltage

When η is of the order a few millivolts equation 2-24, after expanding the exponentials in $G(\eta)$, neglecting the second term onwards and rearranging takes the form

$$-\frac{1}{\eta} = \frac{2(nF)^2}{RT} \cdot \frac{1}{\frac{1}{C_0 D_0^{1/2}} + \frac{1}{C_R D_R^{1/2}}} \cdot \frac{\tau \delta^{1/2}}{C(E-E_2)} \left(\frac{l}{m}\right)^{1/2} \left[1 - \frac{1}{\lambda} \ln(1+\lambda)\right] \quad (2-31)$$

with

$$\lambda = \frac{\pi r \delta^{1/2}}{nF} \left[\frac{1}{C_0^* D_0^{1/2}} + \frac{1}{C_R^* D_R^{1/2}} \right] \left(\frac{l}{m} \right)^{1/2} I_a^0 \quad (2-32)$$

For diffusion control with $\lambda \rightarrow \infty$, $\left[1 - \frac{1}{\lambda} \ln(1+\lambda) \right] \rightarrow 1$, we get

$$-\frac{1}{\eta} = \frac{2(nF)^2}{RT} \frac{1}{\frac{1}{C_0^* D_0^{1/2}} + \frac{1}{C_R^* D_R^{1/2}}} \cdot \frac{r \delta^{1/2}}{C(E-E_2)} \left(\frac{l}{m} \right)^{1/2} \quad (2-33)$$

When $\lambda \rightarrow 0$, for pure charge transfer control, the same equation assumes the form,

$$-\frac{1}{\eta} = \frac{nF}{RT} \frac{\pi r^2 \delta}{C(E-E_2)} I_a^0 \left(\frac{l}{m} \right) \quad (2-34)$$

Thus we see that for small overvoltages $(1/\eta)$ is proportional to $(1/m)^{1/2}$ for pure diffusion control and to $(1/m)$ for pure charge transfer control.

g) Slope-Intercept Analysis of Data

It is shown in the Appendix 3 that for small overvoltages the $(1/m)^{1/2} - (1/\eta)$ relationship can be written as

$$\frac{d(1/m)^{1/2}}{d(1/\eta)} = -\frac{P}{Q} \frac{C(E-E_2)}{r \delta} \left[1 + \frac{1}{P I_a^0} (m/l)^{1/2} \right] \quad (2-35)$$

$$\text{where } P = \pi r^2 \left(\frac{1}{C_0^* D_0^{1/2}} + \frac{1}{C_R^* D_R^{1/2}} \right) \quad (2-36)$$

$$\text{and } Q = \frac{2\pi r nF}{RT} \quad (2-37)$$

It can be seen from the equation 2-35 that a linear plot of the derivation $d(1/m)^{1/2}/d(1/\eta)$ against $(m/l)^{1/2}$ should give

$$\text{Intercept} = -\frac{RT}{2(nF)^2} \left[\frac{1}{C_0^* D_0^{1/2}} + \frac{1}{C_R^* D_R^{1/2}} \right] \frac{C(E-E_2)}{r \delta^{1/2}} \quad (2-38)$$

and

$$\text{Slope} = - \frac{RT}{nF} \frac{c(E-E_z)}{2\pi r^2 \delta} \cdot \frac{1}{I_a} \quad (2-39)$$

hence

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{\pi F}{\pi r \delta^{1/2}} \frac{1}{\frac{1}{C_o D_o^{1/2}} + \frac{1}{C_R D_R^{1/2}}} \cdot \frac{1}{I_a} \quad (2-40)$$

The quantities c and E_z need not be known in this method and the analysis is then simplified.

CHAPTER III

EXPERIMENTAL METHODS

1) Solutions

All the chemicals used were of Analytical Reagent Grade. The chemicals were used from freshly opened bottles without any purification. Double distilled water was used in the preparation of all solutions.

A stock solution mercurous nitrate of 0.1 M strength was made in perchloric acid of known strength. The concentration of mercury in the stock solution was determined by electrogravimetry. For experiments described in Section 3, the concentration of mercuric and mercurous nitrate in the stock solutions were of the order of 1 mM, to minimise hydrolysis. The mercurous nitrate solution contained 0.001 M perchloric acid. The amount of mercury in these solutions were determined by adding a known excess of standard solution of sodium salt of E.D.T.A. and back titrating the excess with zinc solution of known concentration using Eriochrome Black T as indicator at pH around 10.

Approximately a tenth molar solution of vanadyl sulfate was the stock solution of vanadium. Desired concentrations of V(II) and V(III) were obtained by

electrolytically reducing a known amount of vanadyl sulfate in 1 M perchloric acid, using a mercury cathode and a platinum anode in an isolated cell. A potentiostat built in this laboratory was used for electrolysis. Reduction and transfer of solutions were done in an atmosphere of purified nitrogen. The concentrations of V(II) and V(III) were determined polarographically, from the diffusion currents and the capillary characteristics. The diffusion current constant for V(III) was taken as 1.41 from literature.¹

The stock solution for Cr(III) was prepared by reducing a known amount of potassium dichromate with hydrogen peroxide and concentrated hydrochloric acid and boiling the solution for two hours to decompose the excess of hydrogen peroxide. For individual experiments, a known amount of this solution was reduced in separatory funnel with zinc amalgam, shaking the solution for two minutes. By this the entire Cr(III) was reduced to Cr(II). The amalgam was removed and the solution was transferred to the cell in an atmosphere of pure nitrogen. The desired ratio of Cr(II) to Cr(III) was then obtained by controlled aeration.

¹J. J. Lingane, "Polarographic Characteristics of Vanadium in Its Various Oxidation States", J. Am. Chem. Soc., 67, 182 (1945).

The ratio of Cr(II) to Cr(III) was monitored with a dropping mercury electrode.

The zinc amalgam for the streaming amalgam electrode was prepared by reducing 250 ml of 20 mM zinc sulfate solution in sulfuric acid on 250 ml of pure mercury. The electrolysis was carried for overnight to remove all the zinc from the solution. A potentiostat was used for high current delivery. Since the electrolysis was carried to completion it was easier to calculate the concentration of the amalgam.² The electrolysis and the transfer of the amalgam were carried in a nitrogen atmosphere. The amalgam in the reservoir was covered with a small amount of dilute sulfuric acid and was kept negatively polarised until actual use. The connecting tube from the reservoir to the capillary was made of "Teflon" to prevent the oxidation of amalgam due to air seepage, usually observed with tygon tubings.

²N. H. Furman and W. C. Cooper, "A Study of the Polarographic Behavior of Amalgam Electrodes", J. Am. Chem. Soc., 72, 5667 (1950).

2) Apparatus

a) Cell

The cell used (Fig. 3) was a modified form of the one used by Heyrovsky and Forjet³ for the study of the streaming mercury electrode. As the jet carries the solution along with it the level of the solution tends to change continuously. To prevent this the side arm of the cell was connected to the main body by a 7 mm.-glass tubing so that the solution finds its level always. The solution in the side arm was held in by tapering the arm to a capillary and bending it to a reversed S-shape. The mercury collected at the bottom of the bend acted as a seal while permitting at the same time the determination of the mass flow rate of mercury, due to the hydrostatic pressure. There were nitrogen inlets in both parts of the cell. The capillary was introduced from the top of the cell through a stopper.

b) Mercury Jet

The mercury jet was produced by forcing mercury from a reservoir of varying heights, through a precision

³J. Heyrovsky and Forjet, "Oszillographische Polarographie", Z. Physik. Chem., 193, 83 (1943).

Fig. 3 - Cell and capillary of the streaming mercury electrode.

bore⁴ capillary about 2 cm. long attached to a 7 mm inner diameter glass tubing. The glass tubing was bent at the bottom approximately 30° to the vertical, turning upwards.

c) Electrometers

Hewlett Packard Model 425 A microvolt meter (input impedance 1 megohm), Keithley 600 A (battery operated, input impedance 10^{14} ohms on the volts position) and Keithley 150 A (input impedance 9×10^7 ohms) electrometers were used for the measurement of overvoltages. Equilibrium potentials were measured with the usual student potentiometer setup.

d) Measurements

Though it is uncertain at which point the continuous solution film on the moving mercury jet breaks, it can be assumed that under the experimental conditions the solution film breaks at the cone of the solution level-jet interface. It was verified that the breaking of the mercury jet with a flat glass head up to the immediate vicinity of the solution level had no effect on the meter reading. This cone could be clearly seen

⁴Precision bore glass capillaries manufactured by Wilmad Glass Co., Inc. Buena, New Jersey.

when the cell was coated with "Desicote", a water repellent coating for glasswares marketed by Beckman, because of the absence of the meniscus. The apparent length of the jet was measured from the tip of the capillary to the apex of the cone with a cathetometer⁵ to one tenth of a millimeter. Care was taken to see that the capillary-support tubing was always vertical, by keeping the horizontal crosswire of the eyepiece in the plane of the solution level and adjusting the glass support to be parallel to the vertical crosswire. The angle of the bend was measured by projecting the capillary on paper. The true length of the jet was calculated from the cosine of the angle.

The capacity data used in this work were taken from the literature and wherever so used proper references are given. However, for 1 M potassium thiocyanate solution the differential capacity values at various potentials were measured at 1000 Hz with the impedance bridge built in this laboratory. The integral capacities were calculated from the charge obtained by graphical integration using equation 1-5 for various potentials.

⁵Made by Griffin George Ltd., London, U. K.

The electrocapillary curves were used to determine the point of zero charge. The curves were drawn by measuring the average drop life of twenty drops of a dropping mercury electrode at different potentials in the medium concerned. The electrocapillary maximum was determined in the following manner. The potentials with equal drop time were joined by straight lines. The midpoint of such straight lines were joined through another straight line and extrapolated to meet the maximum of the curve and the intersection taken as E_z . All our potentials were referred to this so determined point of zero charge, because the salt-bridge, reference electrode and the arrangements were the same as in the actual study of the electrode process.

In the measurement of the double layer capacity with the streaming mercury electrode in perchloric acid solution, the zero current potential was used as the reference potential E_z , for this involved no extra experimental measurement.

The Sargent Model XV with I. R. Compensator Model A was used in polarographic analysis.

All experiments were conducted at room temperature, around 24°C . The maximum variations were less than two degrees. The average temperature was near 27°C when studies were made with zinc amalgam.

CHAPTER IV

DESCRIPTION AND DISCUSSION OF RESULTS

The experimental results are presented along with the discussion. For the convenience of reference some of the equations as derived in chapter II are given along with.

1) Capacity Current

According to equation 2-12 the capacity current

$$i_c = |c (E - E_2) \frac{2\pi}{76} | \quad (4-1)$$

The initial experiments were conducted to verify this equation. The capacity current should be independent of the length of the mercury jet, and it should be possible to determine the integral capacity from capacity current measurements. Perchloric acid solutions of strength 1 M and 0.01 M were chosen so that the capacities so determined could be compared with those reported by Grahame¹ by his a.c. method. Normal polarographic runs were made with a recorder.

The capacity currents for the streaming mercury electrode were recorded for different mass flow rates

¹D. C. Grahame, "The Electrical Double Layer and the Theory of Electrocapillarity", Chem. Rev., 41, 441 (1947).

of mercury in perchloric acid solutions. When the length of the jet was about 1 mm discontinuity was observed sometimes in the i - E curves near the zero current region. This effect was already observed by Heyrovsky et al.² and Valenta³ who accounted for it by nonwetting of mercury in the absence of a depolariser when the mass flow rate was slow and the length of the jet was short. It was made certain in our experiments that the jet was completely wet as it left the surface of the solution, by keeping the length of the jet more than 3 mm. The discontinuity was not observed then.

The length of the jet was varied from 5 mm to 9 mm and it was found that the capacity current did not vary appreciably, as should be the case.

From the i - E curves for various flow rates m , i_c values were plotted against m for fixed values of $(E-E_z)$. The slope then should correspond to $\frac{2c(E-E_z)}{75}$. Such plots are shown in Fig. 4 for 0.01 M perchloric acid solution. From the slope and the radius of the capillary the capacity was calculated for the particular value of $(E-E_z)$.

²J. Heyrovsky, F. Sorm and J. Forjet, "Capacity Phenomena Displayed at Mercury Capillary Electrodes", Coll. Czechoslov. Chem. Commun., **12**, 11 (1947).

³P. Valenta, "Studium der an der Strömenden Quecksilber-Elektrode auftretenden Stromdiskontinuität", Coll. Czechoslov. Chem. Commun., **16**, 239 (1951).

Fig. 4 - Determination of interfacial capacity from the measurement of capacity current i_c with the streaming mercury electrode at different mass flow rates (m) at fixed potentials with respect to the point of zero charge. The numbers on the slopes correspond to $(E-E_z)$ in volts.

Comparison is made in Fig. 5 between the experimentally determined capacity values and the integral capacities obtained from graphical integration of the differential capacities reported by Grahame. The values calculated from Grahame's paper are represented by the solid line.

It appears that there is fairly good agreement on the positive side of the point of zero charge. On the negative side oxygen might be interfering, though the experiments were carried out with deaerated solutions.

2) General Case: Mixed Control by Mass Transfer and Charge Transfer

$V(II)-V(III)$ couple was chosen for this study. This reaction is known to be controlled both by mass transfer and charge transfer. The rate constant is also known from earlier studies with different techniques. The overvoltage in such a system could be varied by changing the total concentration of vanadium and also the ratio of $V(II)-V(III)$. In the later part of this chapter the study with streaming zinc amalgam electrode is reported for the case of small overvoltage only.

The analysis of the general equation 2-24 is divided into two parts. It simplifies to equation 2-31 for small overvoltages.

Fig. 5 - Comparison between the data obtained with the streaming mercury electrode and those of Grahame. Grahame's data are shown by the solid continuous lines.

a) Large Overvoltage

The relationship expressed in equation 2-24 was verified for equimolar ratio (2.58 mM) of V(II) and V(III). The overvoltages measured were more than 20 millivolts. In the plot of Fig. 6 the ordinate represents

$$\log \lambda \frac{\pi F}{RT \delta^{1/2}} \frac{1}{(1/C_0 D_0^{1/2}) + (\exp(\frac{\pi F \eta}{RT}) (\frac{Q}{M})^{1/2} / C_R D_R^{1/2})}$$

and the abscissa . The diffusion coefficients for V(II) and V(III) were taken as 8.12×10^{-6} and $5.38 \times 10^{-6} \text{ cm}^2 \text{ sec.}^{-1}$ respectively.⁴ The radius of the capillary was $6.25 \times 10^{-3} \text{ cm}$. From the intercept I_a^0 was calculated. The transfer coefficient was found from the slope. The extrapolation from 20 mv region to the ordinate might be a little presumptuous, but considering the general behaviour of the plot one can see that the equation still holds good. We obtained:

$$\alpha = 0.53 \text{ and } k = 4.42 \times 10^{-3} \text{ cm. sec.}^{-1}.$$

b) Small Overvoltage

For $\eta \leq 5 \text{ mv}$ the general equation simplifies to

$$-\frac{1}{\eta} = \frac{2\pi F}{RT} \frac{\pi F}{RT} \frac{1}{\frac{1}{C_0 D_0^{1/2}} + \frac{1}{C_R D_R^{1/2}}} \frac{RT \delta^{1/2}}{C(E-E_0)^{1/2}} \left(\frac{Q}{M} \right)^{1/2} \left(1 - \frac{1}{\lambda} \ln(1+\lambda) \right) \quad (4-2)$$

⁴J. Lingane and L. Meites, "Polarographic Characteristics of 2 and 3 Vanadium I. Polarography in Non-complexing Solutions", J. Am. Chem. Soc., 70, 2525 (1948).

Fig. 6 - Plot for mixed control, large overvoltage.
2.58 mM each of V(II) and V(III) in 1 M
perchloric acid.

and

$$\lambda = \frac{\pi r \delta^{1/2}}{nF} \left[\frac{1}{C_o D_o^{1/2}} + \frac{1}{C_R D_R^{1/2}} \right] \left(\frac{l}{m} \right)^{1/2} I_a^o \quad (4-3)$$

In tables I, II, and III the experimental values of η for different mass flow rates and the length of the jet are given for the solutions under investigation. As described earlier, the values of λ were found by interpolation in the plot in Fig. 2. A plot was made to determine the slope of the λ vs. $(l/m)^{1/2}$ relation from which I_a^o was calculated. One such plot is shown in Fig. 7 for equimolar ratio of V(II) - V(III). Keeping the total concentration of vanadium constant at 30.9 mM, the ratio was varied and the corresponding I_a^o was calculated. The values of I_a^o for different ratios are given in table IV.

Since one has

$$I_a^o = nFk C_o^{(1-\alpha)} C_R^\alpha \quad (4-4)$$

there follows

$$\log \left(\frac{I_a^o}{C_o} \right) = \log nFk + \alpha \log \left(\frac{C_R}{C_o} \right) \quad (4-5)$$

A plot of $\log I_a^o$ vs. $\log (C_R^o/C_o^o)$ was made (Fig. 8) and from the intercept and the slope k and α were calculated. We obtained the values $k = 5.69 \times 10^{-3}$ cm. sec.⁻¹ and $\alpha = 0.56$ which are in fair agreement with

TABLE I

Mixed Control by Mass Transfer and Charge Transfer

Vanadium total concentration 30.9 mM in 1 M perchloric acid
 $V(II) : V(III) = 1 : 1$

l in cm.	m gm. sec. ⁻¹	cm. sec. gm. ⁻¹	$-\eta$ mv.	λ
0.696	0.255	2.73	2.45	0.53
0.466	0.277	1.68	3.5	0.46
0.366	0.267	1.37	4.2	0.41
0.388	0.306	1.27	4.5	0.39
0.278	0.295	0.94	6.	0.33

$$C = 25 \mu F \text{ cm.}^{-2} (E - E_z) : 0.11 \text{ volt} \quad r = 6.25 \times 10^{-3} \text{ cm.}$$

TABLE II

Mixed Control by Mass Transfer and Charge Transfer

Vanadium total concentration 30.9 mM in 1 M perchloric
acid VII) : V(III) = 1 : 5

l cm.	m gm. sec. ⁻¹	$1/m$ cm. sec. gm. ⁻¹	$-\eta$ mv	λ
1.16	0.316	3.67	4.4	0.67
0.887	0.289	3.07	5.	0.61
0.854	0.261	3.27	5.1	0.59
0.748	0.261	2.87	5.8	0.54
0.704	0.289	2.44	6.3	0.55

$$C = 25 \mu F. \text{ cm}^{-2} (E - E_z) = 0.16 \text{ volt} \quad r = 6.25 \times 10^{-3} \text{ cm}$$

TABLE III

Mixed Control by Mass Transfer and Charge Transfer

Vanadium total concentration 30.9 mM in 1 M perchloric acid. V(II) : V(III) = 5 : 1

l cm.	m gm. sec. ⁻¹	l/m cm. sec. gm. ⁻¹	$-\eta$ mv.
0.629	0.32	1.97	0.78
0.493	0.32	1.54	0.94
0.487	0.32	1.52	1.04
0.388	0.364	1.06	1.2
0.329	0.364	0.903	1.28
0.286	0.364	0.886	1.3
0.275	0.364	0.863	1.4
0.32	0.345	0.721	1.7

$$r = 6.25 \times 10^{-3} \text{ cm.}$$

Values are not given because of the high uncertainty involved in the value of $(E-E_z)$ near the electrocapillary maximum. The slope-intercept method was used to find I_a^0 .

TABLE IV

Exchange Current Density for Different Ratios of V(II)
and V(III)

$C_{V(III)}^0 \times 10^6$ moles ml. ⁻¹	$C_{V(II)}^0 \times 10^6$ moles ml. ⁻¹	$I_a^0 \times 10^3$ amp. cm. ⁻²
25.9	5.16	5.33
15.5	15.5	9.33
5.16	25.9	6.57

Fig. 7 - Determination of exchange current density from the λ vs. $(l/m)^{1/2}$ plot. Total concentration of vanadium 31 mM. Equimolar ratio of V(II) and V(III) in 1 M perchloric acid.

Fig. 8 - Plot to determine the rate constant and the transfer coefficient for V(II) - V(III) couple in 1 M perchloric acid.

those reported by Randles^{5,6} ($k = 4.1 \times 10^{-3}$ cm. sec.⁻¹ and $\alpha = 0.5 - 0.57$).

c) Slope-Intercept Method

It has been shown in the derivation of equation 2-40 that one can obtain the exchange current density directly from the $1/\eta$ vs. $(1/m)^{\frac{1}{2}}$ plot. This method is particularly useful when there is uncertainty in the value of $(E-E_z)$. A plot was made between $1/\eta$ and $(1/m)^{\frac{1}{2}}$ and the curve was differentiated at chosen points.

In the tables V and VI the derivatives at the chosen points are given for solutions with 31 mM and 20.5 mM total concentration of vanadium with equal amounts of V(II) and V(III). A plot of the slope was made against $(m/l)^{\frac{1}{2}}$ in Fig. 9. Then according to equations 2-39 and 2-40

$$\text{Slope} = -\frac{RT}{nF} \frac{c(E-E_z)}{2\pi r^2 \delta} \frac{1}{I_a^0} \quad (4-6)$$

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{nF}{\pi r^2 \delta^{\frac{1}{2}}} \frac{1}{\frac{1}{C_0 D_0^{\frac{1}{2}}} + \frac{1}{C_2 D_2^{\frac{1}{2}}}} \frac{1}{I_a^0} \quad (4-7)$$

So I_a^0 could be calculated from either 4-6 or 4-7. The I_a^0 so calculated are given in the table VII.

⁵J. Randles, "The Determination of Kinetic Parameters of Redox Reactions from Current-Potential Curves", Can. J. Chem., **37**, 238 (1959).

⁶J. Randles and K. Sommerton, "Kinetics of Rapid Electrode Reactions", Trans. Faraday Soc., **48**, 937 (1952).

TABLE V

Slope-Intercept Analysis: Tangent Values

Vanadium total concentration 31 mM in 1 M perchloric
acid V(II) : V(III) = 1 : 1

$(1/m)^{\frac{1}{2}}$	$(m/1)^{\frac{1}{2}}$	-Tangent $d(1/m)^{\frac{1}{2}}/d(1/\eta)$
1.	1.	4.
1.1	0.91	3.61
1.2	0.84	3.53
1.3	0.77	3.32
1.4	0.72	3.16

TABLE VI

Slope-Intercept Analysis: Tangent Values

Vanadium total concentration 20.7 mM in 1 M perchloric
acid V(II) : V(III) = 1 : 1

$(1/m)^{\frac{1}{2}}$	$(m/l)^{\frac{1}{2}}$	- Tangent $d(1/m)^{\frac{1}{2}}/d(1/\eta)$
1.	1.	6.44
1.1	0.91	6.
1.2	0.84	5.72
1.3	0.77	5.46
1.4	0.72	5

TABLE VII

Slope-Intercept Analysis: Rate Constants

Vanadium equimolar ratio as V(II) and V(III).

C in mM	-Intercept	-Slope	$k_a^0 \times 10^3$	$k_a^0 \times 10^3$
Tot. concn.	$\times 10^3$	$\times 10^3$	from slope	from slope/ intercept
31.	1.	3.	5.92	4.8
20.7	2.25	4.2	9.53	5.12

Fig. 9 - Slope-Intercept analysis: The ordinate represents $d(l/m)^{1/2}/d(l/\gamma)$. The plots are for equimolar ratio of V(II) and V(III) with 20.7 mM and 31 mM total concentration of vanadium in 1 M perchloric acid.

3) Mass Transfer Controlled Process

For a purely diffusion controlled process, one can assume $I_a^0 \rightarrow 0$ and hence $\lambda \rightarrow 0$. So we get

$$(E-E_z) \left[\frac{\frac{1}{C_o^o D_o^{1/2}} + \frac{1}{C_R^o D_R^{1/2}} \exp \frac{\eta F \eta}{RT}}{[1 - \exp \frac{\eta F \eta}{RT}]} \right] = \frac{2 \eta F r \delta^{1/2}}{C} \left(\frac{l}{m} \right)^{1/2} \quad (4-8)$$

For an electrode reaction involving mercurous ions on mercury electrode the term $1/C_R^o D_R^{1/2}$ is equal to zero.

For low overvoltages (less than 5 mv) the exponent can be approximated by series expansion and taking only the first term. Finally by rearrangement we get,

$$-\frac{1}{\eta} = 2 \eta F \frac{\eta F}{RT} \frac{r \delta^{1/2}}{(E-E_z)} \frac{C_o^o D_o^{1/2}}{C} \left(\frac{l}{m} \right)^{1/2} \quad (4-9)$$

Different concentrations of mercurous ions in 1 M perchloric acid solution as the supporting electrolyte were studied with the streaming mercury electrode. Two different capillaries were used to verify the equations in two independent series of experiments. The data are summarized in tables VIIIa, VIIIb, and IX for both cases, viz. large overvoltage and small overvoltage. In Figs. 10 and 11 $\frac{1}{\eta}$ was plotted against $(l/m)^{1/2}$. From the slope the capacitance of the interface was calculated for that particular potential region and concentration of mercurous ions. It can be seen from the plots that the assumption that the capacitance is fairly constant in the potential region holds well. But the slopes were found not proportional to the concentration

TABLE VIII(a)

Large overvoltage and diffusion control : Hg(I) in 1 M perchloric acid. Capillary radius 7.5×10^{-3} cm.

Concn. Hg_2^{+2} mM	m gm. sec^{-1}	l cm.	overvoltage $-\eta$ mv
1.03	0.55	1.19	7.2
1.03	0.44	1.19	5.65
1.03	0.4	0.72	7.45
1.03	0.51	0.72	8.2
1.03	0.54	0.72	9.55
0.52	0.37	1.08	13.3
0.52	0.48	1.08	17.3
0.52	0.42	0.625	26.5
0.52	0.48	0.625	31
0.52	0.59	0.625	58
0.26	0.39	1.19	88
0.26	0.49	1.19	153
9.26	0.38	0.71	298
0.26	0.47	0.71	342
0.26	0.60	0.75	365

TABLE VIII(b)

Large overvoltage and diffusion control: Hg(II) in 1 M perchloric acid. Capillary radius 6.25×10^{-3} cm.

Concn. Hg_2^{+2} mM	m gm. sec. ⁻¹	l cm.	overvoltage $-\eta$ mv
1.03	0.24	1.14	5.65
1.03	0.29	1.14	6.4
1.03	0.24	0.55	8.95
1.03	0.3	0.55	10.4
0.52	0.23	1.07	12.4
0.52	0.29	1.07	16.0
0.52	0.29	0.59	34.5
0.52	0.225	0.59	23.5
0.26	0.26	0.95	145
0.26	0.30	0.95	190
0.26	0.26	0.71	274
0.26	0.28	0.71	300

TABLE IX

Small overvoltage and diffusion control: Hg(I) in 1 M perchloric acid. Capillary radius 6.25×10^{-3} cm.

Concn. Hg_2^{+2} mM	m gm. sec. ⁻¹	l cm.	overvoltage $-\eta$ mv
10.0	0.196	0.607	0.96
10.0	0.188	0.463	1.1
10.0	0.218	0.455	1.15
10.0	0.181	0.337	1.25
10.0	0.198	0.342	1.51
5.0	0.187	0.805	1.52
5.0	0.187	0.728	1.65
5.0	0.219	0.629	1.91
5.0	0.198	0.446	2.15
5.0	0.217	0.377	2.53
5.0	0.199	0.321	2.56
5.0	0.180	0.263	2.75
2.5	0.218	1.046	2.63
2.5	0.214	0.77	2.93
2.5	0.204	0.653	3.1
2.5	0.200	0.506	3.7
2.5	0.210	0.452	4.07
2.5	0.208	0.373	4.6
2.5	0.218	0.333	5.1

Fig. 10 - Mass transfer controlled process, large over-voltage. Reduction of Hg(I) in 1 M perchloric acid. Two different capillaries were used to verify the relation. Lines a and b, c and d, e and f correspond to 1.03, 0.56 and 0.28 mM Hg(I) , respectively.

Fig. 11 - Mass transfer controlled process, small overvoltage. Reduction of Hg(I) in 1 M perchloric acid. Lines a, b and c correspond to 10, 5 and 2.5 mM of Hg(I), respectively.

of mercurous ions, whereas such a proportionality would be expected for a constant capacitance. This might be due to the change in the capacity with the change in mercurous ion concentration.

In table X the charge on the interface, as calculated from our experiments are compared against those reported by Koenig et al.⁷ in their study of mercury-solution interfacial tension at equilibrium potentials. In the last column in the same table, the values obtained from Sluyters'⁸ experiments are given. There seems to be a fair agreement among all these values at more positive potentials. In this region the η -values are small as the concentration of mercurous ions are high. This region is also the region of dissolution of mercury in Sluyters' experiments. This marked deviation in the capacity values of the interface away from the equilibrium potential might be associated with the effect of electrode process on the capacity of the double layer.

⁷F. O. Koenig, H. C. Wohlers, and D. Bandini, "The Surface Tension between Mercury and Aqueous Solutions of Mercurous Perchlorate and Mercurous Nitrate", paper presented at the Moscow C.I.T.C.E. meeting (1963).

⁸M. Sluyters-Rehbach and J. H. Sluyters, "The Double Layer Capacity of the Mercury-1 M HClO₄ Solution Interface at High D. C. Potentials", Rec. trav. chim., 83, 217 (1964)

TABLE X

Comparison of data: Mercurous ions in 1 M perchloric acid

Potential ($E-E_z$) volts	Concentra- tion mM	Ours	Koenig's	Charge in coulombs, cm^{-2} Sluyters'*
1.05	10	35.3	33.4	-
1.04	5	33.7	-	-
1.03	3.16/2.5	29.4	30.1	-
1.02	1	-	26	27.8
1.01	0.32	-	21.8	-
0.99	0.1	17.4	-	-
0.97	1	20.2	-	24.5
0.94	0.52	-	-	23

* Sluyters' experiments were done with a bulk concentration of 0.4 mM Hg_2^{+2} in 1 M perchloric acid and the potential was adjusted to the values listed in the first column.

4) Charge Transfer Process

The Cr(II) - Cr(III) reaction in potassium chloride solution is controlled by charge transfer. For such a process equation 2-30 can be written as

$$\frac{(E-E_2) \exp \frac{nF\eta}{RT}}{(1 - \exp \frac{nF\eta}{RT})} = \frac{\pi r^2 \alpha}{c} I_a^0 \left(\frac{l}{m} \right) \quad (4-10)$$

Assuming that I_a^0 and α are constant for a given ratio of Cr(II) to Cr(III) one can write

$$\eta = \frac{RT}{nF} \ln \left\{ \frac{(1 - \exp \frac{nF\eta}{RT})}{(E-E_2)} \left(\frac{l}{m} \right) \right\} + \frac{RT}{nF} \ln \left\{ \frac{\pi r^2 \alpha I_a^0}{c} \right\} \quad (4-11)$$

So by plotting η against $\log \left\{ \frac{(1 - \exp \frac{nF\eta}{RT})}{(E-E_2)} \left(\frac{l}{m} \right) \right\}$ one gets a straight line, from the slope and the intercept of which I_a^0 and α can be calculated. The value of capacity c corresponding to the mean E was taken from Parsons' tables.⁹ But the small range of potential, the difficulties related to the choice of E_2 and other experimental errors did not allow the precise determination of α and I_a^0 . A further uncertainty, associated with the determination of I_a^0 , resulted of the long extrapolation.

To minimize this error, the value of α alone was determined experimentally as shown in Fig. 12 for different ratios of Cr(II) to Cr(III) and for different

⁹Private communication.

Fig. 12 - Charge transfer controlled process:
 Cr(III) - Cr(II) in 1 M potassium chloride.
 Determination of α from the slope. The
 Cr(III) - Cr(II) ratio is given on the
 slopes. ○ ■ and ● correspond to 0.1, 0.04 and
 0.04 M total Cr respectively.

total concentrations of Cr(II) Cr(III). Different values were obtained and the mean value was chosen. With this the left-hand-side of equation 4-10 was plotted against $(1/m)$. These plots for some concentrations are shown in Fig. 13. They all pass through the origin as they should. From the slopes values of I_a^0 , and hence of k_a^0 , were calculated and these are shown in the table XI.

In the literature there is no reference regarding the value of α for this reaction. Randles and Sommerton⁶ reported a value $k_a^0 = 1.0 \times 10^{-5} \text{ cm. sec}^{-1}$ which is one order of magnitude smaller than ours.

5) The Streaming Amalgam Electrode

The equations derived in chapter II are equally true for the streaming amalgam electrodes. The validity of the equation for the general case (mixed control) for lower overvoltages was checked for the streaming zinc amalgam electrode in zinc sulphate solutions in 1 M potassium chloride and 1 M potassium thiocyanate solutions as supporting electrolyte.

The diffusion coefficient for zinc in zinc amalgam was taken as $16.7 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ and that of zinc in aqueous solutions as $7.2 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$.¹⁰ The

¹⁰N. H. Furman and W. C. Cooper, "A Study of the Polarographic Behaviour of Amalgam Electrodes", J. Am. Chem. Soc., 72, 5667 (1950).

Fig. 13 - Charge transfer controlled process: Cr(III) - Cr(II) in 1 M potassium chloride. Determination of I_a^0 from the slope. The Cr(III) - Cr(II) ratio is given on the slopes.

TABLE XI

Charge transfer controlled process: Cr(II) to Cr(III) in
1 M potassium chloride. Capillary radius 7.5×10^{-3} cm.

Total Concn. moles/liter	$\frac{\text{Cr}^{+2}}{\text{Cr}^{+3}}$	α by plot	$k_a^0 \times 10^4$ cm. sec. ⁻¹
0.1	4.5	0.5	0.95
0.1	1.9	0.64	1.4
0.1	0.31	0.78	2.2
0.1	0.22	0.5	1.6
0.1	0.17	0.78	1.8
0.04	12	0.59	2.1
0.04	4.2	0.54	1.7
0.04	2.3	0.57	1.8
0.04	1.3	0.58	1.7
0.04	0.77	0.51	1.9
0.04	0.49	0.6	2.2
0.04	0.28	0.66	2.0
0.04	0.12	0.79	2.3

differential capacity data for KCl medium was taken from Parson's work.⁹ Those for KCNS medium were experimentally obtained by the author by the bridge method.

As before, the different methods of analysis for lower overvoltages were carried out for three different concentrations of zinc in each medium. The data are summarized in tables XII and XIII. The rate constant k and the transfer coefficient α were determined by the $\log\left(\frac{I_a}{C_0}\right)$ plot against $\log\left(\frac{C_a}{C_0}\right)$. The plots are shown in Figs. 14 and 15.

For the KCl medium we obtained $k = 4.1 \times 10^{-3} \text{ cm. sec}^{-1}$ which compared favorably with the one reported by earlier workers⁶ ($k = 4.0 \times 10^{-3} \text{ cm. sec}^{-1}$) but the value,

$\alpha = 0.72$, was quite high, i.e. more than twice the value reported hitherto. Similar observations abnormal values of α were obtained by Slotter¹¹ in his study of streaming zinc amalgam electrode.

A value of $k = 1.6 \times 10^{-2} \text{ cm. sec}^{-1}$, and $\alpha = 0.54$ was obtained for this electrode reaction in KCNS medium. The earlier reported value was $k = 1.7 \times 10^{-2} \text{ cm. sec}^{-1}$.⁶

¹¹H. D. Slotter, "Kinetic Study at the Streaming Mercury Electrode", dissertation, University of Michigan, 1960; microfilm Mic 602058, University Microfilms, Inc., Ann Arbor, Michigan.

TABLE XII

Streaming amalgam electrode: zinc in 1 M potassium
chloride Exchange current density

$C_{\text{Zn(II)}}^0$ mM/liter	$C_{\text{Zn(Hg)}}^0$ mM/liter	$I_a^0 \times 10^2$ amp/cm ²
20	20	1.57
10	20	1.3
5	20	1.08

$$r = 6.25 \times 10^{-3} \text{ cm. } D_{\text{Zn(II)}} = 7.2 \times 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}.$$

$$D_{\text{Zn(Hg)}} = 1.67 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}.$$

TABLE XIII

Streaming amalgam electrode: zinc in 1 M potassium
thiocyanate - exchange current density

$C_{\text{Zn(II)}}^0$ mM/liter	$C_{\text{Zn(Hg)}}^0$ mM/liter	$I_a^0 \times 10^2$ amp/cm ²
12	20	3.77
8	20	3.53
4	20	2.29

$$r = 6.25 \times 10^{-3} \text{ cm. } D_{\text{Zn(II)}} = 7.2 \times 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}.$$

$$D_{\text{Zn(Hg)}} = 1.67 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}.$$

Fig. 14 - Plot to determine the rate constant k_s^0 and the transfer coefficient α for $\text{Zn(II)}/\text{Zn(Hg)}$ in 1 M potassium chloride.

Fig. 15 - Plot to determine the rate constant k_a^0 and the transfer coefficient α from the intercept and slope for Zn(II)/Zn(Hg) in 1 M potassium thiocyanate.

6) Mass Transfer Control by Diffusion and Migration

The behavior of the electrode could be followed by this technique quite independently of the solution resistance. In this section the apparent diffusion coefficients for Hg(I) and Hg(II) ions were determined from experiments with the streaming mercury electrode in mercury salt solutions with and without supporting electrolyte. Sodium fluoride was used as the supporting electrolyte as it is known to be least adsorbed on the mercury-solution interface.

For very large overvoltages the general equation

$$(E-E_z) \left[\frac{\frac{1}{C_o^o D_o^{1/2}} + \frac{1}{C_R^o D_R^{1/2}} \exp\left(\frac{\eta F}{RT}\right)}{(1 - \exp\left(\frac{\eta F}{RT}\right))} \right] = \frac{2nF\tau\delta^{1/2}}{C} \left(\frac{l}{m}\right)^{1/2}$$

reduces to

$$(E-E_z) = \frac{2nF\tau\delta^{1/2} C_o^o D_o^{1/2}}{C} \left(\frac{l}{m}\right)^{1/2} \quad (4-12)$$

for the reduction of mercury ions, which is purely mass transfer controlled. $(E-E_z)$ is written as $(E_e-E_z)+\eta$. If the variations of overpotentials are assumed not to affect the double-layer capacity very much in the range under study, then it is evident that the η vs. $(1/m)^{1/2}$ relationship should be linear with an intercept at (E_e-E_z) . The apparent diffusion coefficients could be calculated if all the other values are known.

The concentrations of Hg(I) and Hg(II) studied were 0.21 mM and 0.22 mM respectively. As described

in the legends of Figs. 16 and 17, the concentration of the supporting electrolyte was varied from 0 M to 0.1 M. The capacity data were calculated from Russel's tables.¹²

The η vs. $(1/m)^{\frac{1}{2}}$ plots for both mercuric and mercurous ions are shown in Figs. 16 and 17. The validity of this relationship at all concentrations of the supporting electrolyte is strikingly demonstrated by the linear plots, all converging at the same intercept. The slope of the plot increases with the increase in the concentration of the supporting electrolyte, indicating the increase in diffusion rates. Table XIV gives the calculated apparent diffusion coefficients of Hg(I) and Hg(II) ions in different concentrations of supporting electrolyte.

The change in the value of the diffusion coefficients might be attributed to the decrease in the value of transport number, with the increase in supporting electrolyte concentration. It might be pointed out that in relation to the concentration ratio between the reducible ion and the supporting electrolyte, it is highly improbable that the multifold change in the

¹²C. D. Russel, "Charge and Outer Helmholtz Potential for a Mercury Electrode in Aqueous NaF at 25", J. Electroanal. Chem., 6, 486 (1963).

Fig. 16 - Mixed mass transfer control. Reduction of 0.22 mM Hg(II) in different concentrations of sodium fluoride as supporting electrolyte. $\circ$, $\bullet$, $\square$, $\blacksquare$ and $\triangle$ correspond to 0, 0.003, 0.01, 0.03 and 0.1 M sodium fluoride, respectively.

Fig. 17 - Mixed mass transfer control - Reduction of 0.21 mM Hg(I) in different concentrations of sodium fluoride as supporting electrolyte. ○, ●, and Δ correspond to 0, 0.01 and 0.05 M sodium fluoride respectively.

TABLE XIV

Mixed mass transfer controlled: Hg(I) and Hg(II) in sodium fluoride

Concentration of sodium fluoride moles/liter		Diffusion coefficient $\times 10^6$ cm ² sec. ⁻¹	ϕ volts
Hg(II)	0	1.17	0.150*
	0.003	1.81	0.133
	0.01	4.04	0.122
	0.03	5.83	0.100
	0.1	9.6	0.083
Hg(I)	0	0.6	0.114*
	0.01	2.3	0.098
	0.05	7.4	0.08

*The values for solutions without NaF were taken to be the same as that of 0.001 M NaF.

$$r = 6.25 \times 10^{-3} \text{ cm.}$$

diffusion coefficient is due to the reduction in the transport value.

The stability constants for fluoride complexes of mercuric and mercurous ions are reported as $k_1 = 10.7$ and $k_1 = 3.16$ respectively.¹³ Hence the effects due to complexation appear to be negligible. This point is further illustrated by the fact that all the plots for a given mercury ion concentration and different concentrations of sodium fluoride have the same intercept, indicating a constant E_e .

In view of the above discussion, a possible correlation could be that of the ϕ -effect, arising out of the electrical double layer. Since the whole process is taking place on the positive side of the electrocapillary maximum, ϕ is positive and consequently positive mercury ions experience repulsion in the potential gradient resulting in smaller apparent diffusion coefficients. The increase in the supporting electrolyte concentration decreases the ϕ -effect and the value of diffusion coefficient increases. In the table the approximate values of ϕ potentials are given for the median value of η . It should be noted, however,

¹³J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, "Stability Constants of Metal Ion Complexes - Part II", The Chemical Society, London, 1958, p. 91.

that the ϕ -effect concerns only the double layer region whereas our experiments pertain to the much thicker diffusion layer. The ϕ -values probably give a datum characterizing, in a way, the repulsion in the diffusion layer.

The values of D for Hg(II) and Hg(I) are reported as $8.2 \times 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$ and $9.2 \times 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$ respectively in 0.1 M nitric acid. Our values are not too different from these, if one considers the variety of approximations made in calculating the values of c_1 and the slopes.

CHAPTER V

CONCLUSION

The potential of the streaming (or amalgam) electrode at open circuit can be correlated to the kinetics and mass transfer characteristics of the process occurring on the electrode. Since measurements are carried out at open circuit, application to the study of electrode process in media of low conductivity (solvents of low dielectric constants) is conceivable. At least two difficulties would have to be considered in future studies of this type: interference resulting from the variations of potential along the jet and complication arising from migration.

APPENDIX¹

1. Derivation of Equation 2-22

$$dif = \frac{S dl}{\frac{1}{I_a} + N \left(\frac{l}{m} \right)^{1/2}} \quad (A-1)$$

It is required to integrate from the tip of the capillary to the emerging length of the jet.

$$\text{let } \frac{1}{I_a} + N \left(\frac{l}{m} \right)^{1/2} = y \quad \text{therefore } l^{1/2} = \frac{m^{1/2}}{N} \left(y - \frac{1}{I_a} \right)$$

$$\text{then } dy = \frac{1}{2} \frac{N}{(ml)^{1/2}} dl$$

$$\text{and } dl = \frac{2(ml)^{1/2}}{N} dy$$

$$\text{therefore } dl = \frac{2m}{N^2} \left(y - \frac{1}{I_a} \right) dy \quad (A-2)$$

$$\text{It follows } \int_0^l di_f = \int_0^l \frac{S}{y} \frac{2m}{N^2} \left(y - \frac{1}{I_a} \right) dy \quad (A-3)$$

$$i_f = \frac{2Sm}{N^2} [y]_0^l - \frac{2Sm}{N^2 I_a} [\ln y]_0^l \quad (A-4)$$

$$i_f = \frac{2Sm}{N^2} \left\{ N \left(\frac{l}{m} \right)^{1/2} - \frac{1}{I_a} \ln \left[1 + N I_a \left(\frac{l}{m} \right)^{1/2} \right] \right\} \quad (A-5)$$

¹See P. Delahay, "Electrode Kinetics at Open Circuit at the Streaming Mercury Electrode. I. Theory", J. Electroanal. Chem., in press.

$$i_f = \frac{2Sm}{N^2} \frac{1}{I_a} \left\{ \lambda - \ln(1+\lambda) \right\} \quad \begin{matrix} (A-6) \\ (2-22) \end{matrix}$$

where

$$\lambda = N I_a \left(\frac{l}{m} \right)^{1/2}$$

2. Derivation of Equation 2-24 for Steady State Conditions

$$c (E-E_2) \frac{2m}{\tau \delta} = \frac{2Sm}{N} \left(\frac{l}{m} \right)^{1/2} \left[1 - \frac{1}{\lambda} \ln(1+\lambda) \right] \quad (A-7)$$

$$(E-E_2) = \frac{\tau \delta}{c} \frac{S}{N} \left(\frac{l}{m} \right)^{1/2} \left[1 - \frac{1}{\lambda} \ln(1+\lambda) \right]$$

substituting for S and N

$$S = 2\pi r \left[\exp\left(-\frac{\alpha n F}{RT} \eta\right) - \exp\left(\frac{(1-\alpha)n F}{RT} \eta\right) \right]$$

$$N = \frac{\pi r \delta^{1/2}}{n F} \left\{ \frac{\exp\left[-\frac{\alpha n F}{RT} \eta\right]}{C_o^o D_o^{1/2}} + \frac{\exp\left[\frac{(1-\alpha)n F}{RT} \eta\right]}{C_R^o D_R^{1/2}} \right\}$$

$$(E-E_2) = \frac{\tau \delta^{1/2}}{c} \frac{2\pi r}{\pi r \delta^{1/2} n F} \frac{\exp\left[-\frac{\alpha n F}{RT} \eta\right] - \exp\left[\frac{(1-\alpha)n F}{RT} \eta\right]}{\frac{\exp\left[-\frac{\alpha n F}{RT} \eta\right]}{C_o^o D_o^{1/2}} + \frac{\exp\left[\frac{(1-\alpha)n F}{RT} \eta\right]}{C_R^o D_R^{1/2}}} \left(\frac{l}{m} \right)^{1/2} \left(1 - \frac{1}{\lambda} \ln(1+\lambda) \right) \quad (A-8)$$

$$(E-E_2) = \frac{2\tau \delta^{1/2} n F}{c} \frac{\exp\left[-\frac{\alpha n F}{RT} \eta\right]}{\exp\left[-\frac{\alpha n F}{RT} \eta\right]} \frac{(1 - \exp\left(\frac{n F}{RT} \eta\right))}{\left[\frac{1}{C_o^o D_o^{1/2}} + \frac{\exp\left(\frac{n F}{RT} \eta\right)}{C_R^o D_R^{1/2}} \right]} \left(\frac{l}{m} \right)^{1/2} \left(1 - \frac{1}{\lambda} \ln(1+\lambda) \right) \quad (A-9)$$

$$(E-E_2) \frac{\frac{1}{C_o^o D_o^{1/2}} + \frac{\exp\left(\frac{n F}{RT} \eta\right)}{C_R^o D_R^{1/2}}}{\left[1 - \exp\left(\frac{n F}{RT} \eta\right) \right]} = \frac{2n F \tau \delta^{1/2}}{c} \left(\frac{l}{m} \right)^{1/2} \left[1 - \frac{1}{\lambda} \ln(1+\lambda) \right] \quad \begin{matrix} (A-10) \\ (2-24) \end{matrix}$$

3. Derivation of Equation 2-35 for the Slope-intercept Analysis:

The general equation 2-31 for small overvoltages can be written as

$$-\frac{1}{\eta} = \frac{Q}{P^2} \frac{\tau \delta}{c(E-E_2)} \frac{1}{I_a^0} (\lambda - \ln(1+\lambda)) \quad (A-11)$$

where

$$Q = 2\pi r \frac{nF}{RT}$$

and

$$P = \pi r^2 \left(\frac{1}{C_0^0 D_0^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right)$$

also

$$\lambda = P I_a^0 \left(\frac{l}{m} \right)^{1/2}$$

$$\text{Writing } \frac{d(\frac{1}{\eta})}{d(\frac{l}{m})^{1/2}} = \frac{d(\frac{1}{\eta})}{d(\lambda)} \cdot \frac{d(\lambda)}{d(\frac{l}{m})^{1/2}} = P I_a^0 \left(\frac{d(\frac{1}{\eta})}{d\lambda} \right) \quad (A-12)$$

one gets from A-11

$$\frac{d(\frac{1}{\eta})}{d(\frac{l}{m})^{1/2}} = -P I_a^0 \frac{Q}{P^2} \frac{\tau \delta}{c(E-E_2)} \frac{1}{I_a^0} \left[1 - \frac{1}{(1+\lambda)} \right] \quad (A-13)$$

rearranging this

$$\frac{d(\frac{1}{\eta})}{d(\frac{l}{m})^{1/2}} = -\frac{Q}{P} \frac{\tau \delta}{c(E-E_2)} \frac{\lambda}{(1+\lambda)} \quad (A-14)$$

or

$$\frac{d(\frac{l}{m})^{1/2}}{d(\frac{1}{\eta})} = -\frac{P}{Q} \frac{c(E-E_2)}{\tau \delta} \left(1 + \frac{1}{\lambda} \right) \quad (A-15)$$

substituting for λ ,

$$\frac{d(\frac{l}{m})^{1/2}}{d(\frac{1}{\eta})} = -\frac{P}{Q} \frac{c(E-E_2)}{\tau \delta} \left[1 + \frac{1}{P I_a^0} (m/l)^{1/2} \right] \quad \begin{matrix} (A-16) \\ (2-35) \end{matrix}$$

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VITA

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EXAMINATION AND THESIS REPORT

Candidate: Vakula S. Srinivasan

Major Field: Chemistry

Title of Thesis: Electrode Kinetics at Open Circuit at the Streaming Mercury Electrode

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

April 27, 1965