ANALYSIS AND APPLICATION OF CURRENT PULSE TECHNIQUES IN ELECTROCHEMICAL KINETICS

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ABSTRACT

ANALYSIS AND APPLICATION OF CURRENT PULSE TECHNIQUES IN ELECTROCHEMICAL KINETICS

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The determinate errors involved in the various methods of analyzing the data of the current impulse and coulostatic techniques when the relaxations are neither charge transfer nor diffusion controlled are discussed as a function of the ratio of the charge and diffusional time constants τ_c/τ_d . The validity of the application of the simple charge transfer assumption is found to be dependent on an accurate knowledge of the capacitance and on accurate measurements of the potential at short times in the decay. The accuracies of a nomographic and a curve fitting technique of correcting the data for the influences of diffusion are discussed. The accuracy of the first is found to be dependent on an accurate knowledge of the capacitance and short time measurements while that of the second is found to be relatively independent of τ_c/τ_d and the time at which the measurements are made, providing that a sufficient portion of the observed decay is charge transfer controlled.

The current impulse technique is used to study the electrochemical kinetics of the hexacyanoferrate(III)/(II) couple on platinum. Some new instrumentation is developed which compensates the ohmic potential and allows measurements to be made at extremely short times. The exchange rate of the reaction is found to be strongly dependent on the oxidation state of the electrode surface. An oxidized electrode surface state and a reduced electrode surface state are experimentally defined. The reduced exchange rate at oxidized electrodes could be accounted for in terms of a reduction of the "active area" of the electrode. The transfer coefficient and activation energy are not affected by surface oxidation. All experimental evidence points to a simple first order electron transfer reaction in both cases. The results of the investigation are found to be in concordance with those measured by other techniques when surface oxidation effects are taken into account.

The determinate errors involved in the measurement of the exchange current with the galvanostatic technique are examined as a function of τ_c/τ_d . It is found that Delahay's reduced equation for the calculation of the exchange current from the extrapolation of the $\eta \underline{vs}$. $t^{\frac{1}{2}}$ curve to zero time is not valid for the conditions previously reported. A new approach to galvanostatic measurements is suggested which is dependent on high current short time observations. Some new instrumentation for the compensation of ohmic potential is described which allows these measurements to be made. A computer program is developed to analyze the experimental data. Some preliminary results are reported on the hexacyanoferrate(III)/(II) couple.

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ANALYSIS AND APPLICATION OF CURRENT PULSE TECHNIQUES IN ELECTROCHEMICAL KINETICS

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A THESIS

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I. INTRODUCTION TO THE CURRENT IMPULSE TECHNIQUE

A. Description of the Current Impulse Technique

The current impulse technique (1) is a transient perturbation method for the study of rapid electrochemical reactions. The potential of the electrochemical cell is observed in response to a very brief impulse of constant current of precisely defined duration τ , and amplitude i_t, as shown in Figure 1. Because the pulse is of extremely short duration, the transient impedance of the double layer capacitance C_d is small relative to the faradaic resistance R_f (R_f = RT/nFI₀), and the double layer capacitance is charged to some new potential $\eta_{t=0}$, before a significant amount of charge is consumed by the faradaic process.

If the impulse is applied so that the cell is decoupled from the pulse source at the termination of the impulse, the discharge of the excess charge stored in the double layer can take place only through the faradaic process. In the absence of mass transport processes the potential follows a simple exponential decay law with time $\eta = \eta_{t=0} \exp(-t/R_f C_d)$. The

Current Pulse







- C_d Double layer capacitance
- R_f Faradaic resistance
- R_s Solution resistance
- $Z_{m}(t)$ Mass transport impedance

Observed Response



Figure 1

Electrical analog for a current impulse experiment

exchange current I_0 of the reaction can be calculated directly from the slope of the log(n) <u>vs</u>. t curve if we know the capacitance, from the relationship slope = $(nF/2.303RT)(I_0/C_d)$.

There are two ways of obtaining a measure of the double layer capacitance from a current impulse experiment. The $\log(n)$ <u>vs</u>. t curve can be extrapolated to zero time (defined as the time of the termination of the impulse), and the capacitance can then be calculated from the relationship $C_d = i_t \tau / n_{t=0}$. It can also be determined by measuring the slope of the overpotential time curve while charging the double layer with a constant current from the relationship $C_d = i_t/(dn/dt)$. These capacitances are known as the charge and discharge capacitances respectively, and theoretically should have the same value.

When mass transport processes become important, the slope of the log(n) <u>vs</u>. t curve decreases as time proceeds, and it becomes much more difficult to obtain the kinetic parameters from the overpotential time data. Specialized mathematical techniques may be needed to extract the kinetic data from the experimental curves.

B. <u>History of the Current Impulse</u>

and Coulostatic Methods

The principles of the coulostatic technique, which is the historical and logical predecessor to the current impulse technique, were developed independently and simultaneously by Reinmuth (2,3) and Delahay (4-7), though each admitted the priority of the principle of the method to Barker (8,9). The theoretical treatments of the two authors, although from slightly different points of view, lead to essentially the same results. However, Reinmuth's formalism is more elegant and is easier to relate to physical concepts than Delahay's. Both authors considered the problem including mass transport processes, and derived a general equation which they showed could be reduced to two simpler forms when the relaxation was either essentially charge transfer controlled or essentially mass transfer controlled.

The two authors took alternative experimental approaches to the problem of generating a coulombic impulse in a time negligible with respect to the time constant of an electrochemical reaction. Delahay (10) used a simple device consisting of a small, high quality capacitor which was simply shunted across the cell through a system of relays after being charged with a battery to a known voltage. Thus a charge of accurately

known coulombic content q = CV, where C is the capacitance of the capacitor, and V the voltage of the battery, was rapidly injected into the system.

Reinmuth (2) coupled the cell to a fast rise time pulse generator through a small capacitor. Pseudodifferentiation of the leading edge of the pulse by the R-C combination of the cell resistance and coupling capacitor resulted in the application of a coulombic pulse of a magnitude fixed by the pulse voltage and the capacitance of the coupling capacitor. Both of these experimental techniques gave pulses of very short duration but of a rather undefined form.

The major experimental difficulty of these two approaches is the large ohmic drop due to uncompensated solution resistances, which appears throughout the duration of the pulse. This ohmic drop may be many times the magnitude of the relaxation signal, and may drive the amplifiers of the measuring system into saturation. Recovery of the amplifiers from this overdrive may be quite slow. This often prevents the observation of any meaningful relaxation data for several microseconds after the start of the experiment. Since the first portion of the relaxation curve is obscured in many cases by relaxation of the amplifiers and by residual IR drop, the capacitances obtained in this method by extrapolation of the relaxation curve

to zero time are necessarily somewhat uncertain due to the length of the extrapolation. This inability to make accurate short time measurements also limits the rates of the reactions which can be studied to those in which the half times are much greater than the time interval before reliable measurements can be made.

The current impulse technique was conceived by Weir and Enke (1) to minimize some of the experimental difficulties encountered with the coulostatic technique. It is a simple but important modification of the coulostatic technique. Instead of using a charged capacitor to generate the coulostatic pulse, a constant current pulse generator is used.

This produces several significant advantages. When the pulse is applied to the cell, the double layer capacitance charges linearly, and from the slope of this charging curve and the magnitude of the applied current, the capacitance may be calculated. This eliminates the unnecessarily long extrapolations to zero time of the coulostatic method to obtain the capacitance. Second, all ohmic contributions to the measured potential vanish instantaneously upon the cessation of the current pulse, in contrast to the coulostatic case where the charge is injected by a small capacitor. Third, the charge can be injected more rapidly with a constant current generator than with the discharge of

a capacitor. This decreases the amount of the injected charge which is consumed by the faradaic process during the time of the injection. Finally, overdrive of the amplifiers of the measuring system can be eliminated by compensating for the IR drop of the solution, since the form of the perturbing impulse is precisely defined.

These two closely related techniques have been applied to several experimental systems with varying amounts of success. Delahay and Aramata (10) applied the coulostatic technique to the study of the Zn(II)/Zn(Hg) reaction in 1.0M KCl. Hamelin (11,12) used the technique to investigate the Zn(II)/Zn(Hg) reaction in a number of electrolytes, and the Bi(III)/Bi(Hg) reaction (13) in perchloric acid and nitric acid. Wilson (14) investigated the Zn(II)/Zn(Hg) reaction in several concentrations of KCl as the supporting electrolyte, Fe(III)/Fe(II) in 0.1M and in 0.3M oxalic acid, and the Cd(II)/Cd(Hg) reaction in 1.0M KCl and in 1.0M KNO₃. In all cases the results were in reasonable agreement with the theoretically predicted behavior, and with the results of other investigators.

Kooijman (15) conversely concluded that his measurements of the Hg(I)/Hg couple in 1M perchloric acid were essentially meaningless since adsorption processes were involved and the relaxation time constant therefore included not only the double layer capacitance,

but also a pseudo-capacitance which could not be separated from the total capacitance. He also claimed (16) that the reaction was so rapid that mass transport processes dominated the decay and it was therefore difficult to obtain reasonable estimates of the charge transfer parameters.

The current impulse technique has been applied to the electrochemical reduction of the Hg(I)/Hg couple in 1.0M perchloric acid by Weir and Enke (17) and the hexacyanoferrate(III)/(II) system in 1.0M KCl on platinum by Daum and Enke (18). In the first system Weir and Enke found, as Kooijman later found, that the Hg(I)/Hg couple is indeed not only a very rapid reaction but also a very complicated one. Much of the data could not be interpreted unambiguously, and evidence for adsorption and a preceding reaction was obtained. The second system, however, was found to be quite simple with results which agreed well both with theory and with the results of other investigators. This investigation will be discussed in detail in Section III of this thesis.

Other methods based on the idea of the coulostat have been developed. Wilson (14) described a double pulse method for the determination of the half time of a relaxation. The technique consists of the application of two pulses to the system. The second pulse, of

one-half the magnitude of the initial pulse and of opposite sign, is applied at a time such that the potential is returned to its equilibrium value. The time which the second pulse takes to restore the potential to the equilibrium potential is the half-time of the relaxation. Levy (19) developed a small amplitude impulse chain method. The pulses are applied to the system in an evenly spaced train in which successive pulses are of equal magnitude but of opposite sign. The method was used to investigate several systems and good agreement was reported between experiment and theory.

Delahay (20) described a large amplitude technique as an alternate analytical method to polarography. In this method an impulse is applied to the system of such a magnitude that it is perturbed to a potential where the reaction is diffusion controlled. This corresponds to the situation in polarography of rapidly perturbing the system from the foot of the wave to the potential where the current is diffusion limited.

C. <u>Comparison of the Current Impulse Technique</u> <u>With Other Electrochemical Relaxation Techniques</u>

Experimental relaxation methods for the study of electrochemical kinetics can be conveniently divided into two classes, periodic techniques and transient

techniques. In the former the electrochemical cell is perturbed with some periodic variation of the potential and the cell current is observed as a function of time. With transient techniques the response of the cell is observed when the system is perturbed from equilibrium with a step function of either the current or the potential. The comparison of the current impulse method will be limited to a comparison with the common transient relaxation techniques, and will further be restricted to those which are limited to small amplitudes for which the current-voltage characteristic can be linearized.

The first of these techniques is the voltostatic technique (21), in which a voltage step is applied to the cell and the current is observed as a function of time. This method is limited to relatively slow times, and consequently relatively slow processes, because the potential change at the interface is controlled by the time constant of the double layer capacitance and the series resistance of the cell.

A closely related technique is the potentiostatic method (22), in which the electrode potential is perturbed by a fast rise time potentiostatic control system and the current is observed as a function of time. The problem here is essentially the same as that of the voltostatic method. A rapid change of the interface

potential requires a large current to charge the double layer. Therefore, the amount of time which is necessary for the potential to reach its controlled value is dependent on the current output and the rise time of the potentiostat. The best experimental systems which have been devised to date require somewhat more than a microsecond to charge the double layer and permit the accurate observation of the cell current.

With the galvanostatic technique (23) the cell potential is observed in response to the application of a constant current. The problems of this method can be traced to two sources. The first of these is of course the double layer capacitance. Initially a large portion of the applied current goes to the charging of the double layer capacitance, and very little to the faradaic process. It takes a significant amount of time for the cell potential to reach that required by the applied current, and measurements must be obtained at relatively long times with respect to the start of the experiment, and extrapolated back to zero time to obtain the charge transfer overpotential.

The second experimental problem which afflicts the galvanostatic method is the ohmic potential resulting from the solution resistance of the electrochemical cell. This problem is especially acute when studying fast reactions. In these cases high current densities

must be applied to the test electrode in order to obtain measurable values of the charge transfer overpotential. Current densities of this magnitude invariably cause an ohmic potential which is many times the magnitude of the charge transfer overpotential. This unwanted voltage must either be compensated experimentally, or be accurately measured and subtracted from the signal mathematically.

The double pulse galvanostatic method (24) was developed to avoid the double layer charging problem of the galvanostatic method by pre-charging the double layer with a high magnitude short duration current pulse. Experimentally the magnitude of the pre-pulse was adjusted so that the overpotential time curve started with a horizontal tangent at the beginning of the second pulse. Thus it was hoped that the current passing through the cell would be entirely faradaic at that instant. The experimental problems associated with obtaining a pre-pulse of precisely the right magnitude have recently been reconsidered (25), and it has been concluded that the double pulse method offers no significant advantages over the classical galvanostatic method.

The experimental problems of the above techniques are due to the fact that the double layer capacitance is in parallel with the electrode reaction. This

contributes significantly to the morphology of the potential or current characteristic of these methods at a time scale where the most meaningful information on fast reactions exists. Moreover, in the methods which are current perturbed, the signal of interest must be extracted from a total signal which includes the ohmic potential.

With the current impulse technique these experimental difficulties are largely circumvented. Initially, when the double layer is charged, the time scales are so fast that essentially no reaction takes place and the two phenomena are not competing. After the charging process is complete, the only path for the discharge of the excess charge stored in the double layer is through the faradaic reaction to ground. No current is diverted from the reaction to charge the double layer; it is already charged, and the path of its discharge is well defined. Moreover, since no significant current flows through the cell during the relaxation, there is no need to correct the observed overpotentials for the effects of ohmic drop.

There are other significant advantages in using the current impulse technique. One is the inherent simplicity of the experimental apparatus. All that is required in the case of the coulostatic technique is a battery to charge the capacitor, a system of

relays to apply the pulse to the cell, and a moderately fast oscilloscope to observe the potential. The current impulse technique requires only a slightly more complicated high output, fast rise time current pulse generator to perturb the system. Another advantage of the method is its ability to obtain a relatively unambiguous estimate of the double layer capacitance under very reactive conditions.

These characteristics are especially important in the study of film formation reactions. These reactions can be studied as a function of surface coverage, since a known and very small quantity of surface can be applied or removed with each pulse according to its coulombic content and sign. The exchange current and capacitance can be tabulated as a function of the surface coverage. From this information a great deal can be learned about the mechanism of film formation in terms of how these variables change as the surface changes.

D. Limitations of the Current Impulse Technique

The only significant experimental problem of the current impulse method is the overdrive of the amplifier system during the charging process. To minimize the charging time for fast reactions, very high currents and short times are used. These conditions typically

cause ohmic drops of 200 to 500 millivolts, driving the oscilloscope amplifier into saturation. Recovery from overdrive may take up to several microseconds, depending on the oscilloscope and the amount of overdrive. This limits the rate of the reaction which can be studied, as was discussed previously.

The other limitations of the method are of a more theoretical nature. The relaxation curves obtained from this method are featureless monotonic decays, as they are from all relaxation techniques. The experimental decays usually fit any one theoretical model as well as any other. Even when large differences are evident in theoretical decays for the various models, the limited accuracy of the experimentally low level signal usually precludes the adoption of any one theoretical model over any other.

The second theoretical problem is the separation of the charge transfer parameters from experimental relaxations which are predominately mass transfer controlled. With rapid reactions the rate of conversion of reactant to product is so fast that a deficit of reactant and an excess of product is built up at the surface of the electrode, and a diffusion gradient is set up. Ultimately, if the reaction is fast enough, the rate of the decay of potential becomes limited to the rate at which the reactant can diffuse to the

electrode surface. When this happens, the relaxation is diffusion controlled and no kinetic information is available from the decay. This imposes a distinct upper limit on the rate of the reaction which can be studied.

In their original papers Delahay (7) and Reinmuth (3) proposed several conditions which must be satisfied in order for the general equation to be reduced to either the charge transfer or the diffusion limiting equation. Unfortunately, most of the electrochemical reactions which have been studied with this technique produce relaxations which are neither purely charge transfer nor purely diffusion controlled, but a combination of the two.

Weir and Enke (17) and Daum and Enke (18) have said that satisfactory estimates of the charge transfer parameters can be obtained from decays of this type by obtaining the slope of the log(n) <u>vs</u>. t curves at times sufficiently short to apply the simple charge transfer assumption. However this assumption has not been subjected to a rigorous numerical analysis, and correspondingly there has been some concern in the literature about the validity of some of the kinetic parameters which have been obtained by this method (26).

There have been several attempts to correct relaxation data for mass transport phenomena (16,27).

but all of these techniques require a significant amount of tedious calculation, since the arguments of the general function which includes mass transport become complex in the region of greatest experimental interest.

The purpose of Section II of this thesis is to clarify some of the ambiguities involved in obtaining kinetic data from this measurement technique by discussion of some of the determinate errors which are present in the various methods of analyzing the relaxation data as a function of the ratio of the charge and diffusional time constants, and to suggest techniques which experimenters can use to minimize these errors.

II. NUMERICAL AND GRAPHICAL ANALYSIS OF THE DATA OF THE COULOSTATIC AND CURRENT IMPULSE TECHNIQUES

A. Theory

The general equation derived by Reinmuth (3) to describe the decay process is $n = n_{t=0}(\beta_{+} - \beta_{-})^{-1} [\beta_{+}exp(\beta_{-}^{2}t)erfc(\beta_{-}t^{\frac{1}{2}}) - \beta_{-}exp(\beta_{-}^{2}t)erfc(\beta_{+}t^{\frac{1}{2}})](1)$ where

$$\beta_{\pm} = \tau_{d}^{\frac{1}{2}}/2\tau_{c}^{\pm} \frac{1}{\tau_{c}} \tau_{d}^{\frac{1}{2}}}(\tau_{d}^{2}/4\tau_{c}^{2} - 1)^{\frac{1}{2}}$$
(2)

and the charge transfer time constant is

$$r_{c} = RTC_{d}/nFI_{0}$$
 (3)

and the diffusional time constant is

$$r_d = [RTC_d/n^2 F^2 (1/C_0 D_0^{\frac{1}{2}} + 1/C_R D_R^{\frac{1}{2}})]^2.$$
 (4)

Equation 1 reduces to the simple charge transfer equation $\pi = \pi_{t=0} \exp(-t/\tau_c)$ (which is the result which could be obtained if diffusion processes were ignored in the derivation) if $\tau_c >> \tau_d$. If $\tau_d >> \tau_c$, Equation 1 reduces to $\pi = \pi_{t=0} \exp(t/\tau_d) \operatorname{erfc}(t/\tau_d)^{\frac{1}{2}}$, which is the diffusion limiting equation.

It is desirable to make any electrochemical reaction under study conform as closely as possible to the charge transfer limiting equation, since systems

which fulfill this requirement produce the most meaningful information about the electrochemical charge transfer process which is occurring at the interface.

It can be seen from the definition of τ_c and τ_d that the charge transfer limiting equation is favored at high concentrations of electroactive species and low exchange currents. Experimentally a system can be made to conform more closely to the charge transfer limit if the concentrations are increased. Of course, the concentration cannot be increased infinitely because of solubility limitations and because the function of the supporting electrolyte becomes ill defined at high concentrations.

Experimentally, if $\tau_c \gg \tau_d$ and C_d is known, the exchange current can be calculated from the experimental data in a number of simple ways. The first of these is to take the half time of the decay, i.e., the time at which the overpotential is half its initial value, and calculate I_0 from the relationship $t_{\frac{1}{2}} = 0.69315 \tau_c$. The second method is to plot $\log(n)$ <u>vs</u>. t and calculate the exchange current from the slope of the resulting straight line. If $\tau_d \gg \tau_c$, the decay is diffusion controlled, the half time and the slope are independent of the charge transfer parameters, and no kinetic information is available.

When neither of the above inequalities is satisfied, the decay is neither charge transfer nor diffusion

controlled, but is a combination of both. In this case ${}^{\tau}c^{\simeq}{}^{\tau}d$, and the decay is essentially charge transfer controlled at long times. A theoretical relaxation curve with a ${}^{\tau}c/{}^{\tau}d$ ratio of 12.5 is shown in Figure 2. The curves are very close at short times, indicating essential charge transfer control, but deviate substantially at long times, indicating the inception of diffusion control.

B. Graphical Analysis

Kinetic information can be obtained from relaxations of this type in a variety of ways. The simplest and most direct method of estimating the reaction rate is to assume the simple charge transfer limiting equation. The application of this assumption to data of this type obviously presents some difficulties, but these difficulties can be minimized by proper attention to the way in which the measurements are made.

An important consideration for the accuracy of these measurements is the value of the double layer capacitance. There are a variety of methods available for the experimental determination of the capacitance under non-reactive conditions, <u>i.e.</u>, when the electrode is ideally polarized. Many investigators seem to feel that the capacitance for an electrode at a certain potential and in a specified solution should be the

Figure 2

Theoretical decay curves with $C_d = 2 \times 10^{-5} \text{ F/cm}^2$, $\tau_c/\tau_d = 25.0$, $I_0 = 0.18$, n = 1, $D_0 = D_R = 10^{-5} \text{ cm}^2/\text{sec}$, $C_o = C_R = 10^{-5} \text{ moles/cm}^3$. Upper curve calculated assuming general equation, lower curve calculated assuming charge transfer limiting equation.



same regardless of whether the electroactive species is present or not. There is no a priori reason to believe this is true in all cases. For example, if specific adsorption of the electroactive species occurs, then the capacitance may differ widely from its value with no electroactive species. Or if solutions of extremely high concentrations of electroactive species are studied. the capacitance may change because of the addition of these ions to the double layer. Furthermore, in the case of solid electrodes. the value of the capacitance is dependent on small additions of oxide or other films to the electrode surface and is particularly sensitive to the adsorption of any organic compounds. It is important, therefore, to make the measurement of the double layer capacitance in the same solution and at the same time that the relaxation measurement is made.

The value of the capacitance can be estimated from coulostatic data by the extrapolation of the log(n) <u>vs</u>. t curve to zero time. The current impulse method provides an additional estimate from the charging curve, since the charging process is more or less linear. Both of these measurements can involve some very large determinate errors depending on the time at which the measurements are made, the definition of zero time, and the ratio τ_c/τ_d of the charge transfer and diffusional time constants. Initially we will
assume that the capacitance is known, and will calculate errors resulting only from the neglect of mass transport processes in the calculation of the exchange current.

Figure 3 is a graph of the determinate error in the measurement of the exchange current as a function of the ratio $R = \tau_c/\tau_d$. The calculations were made by assuming a diffusional time constant and by systematically varying the exchange current and time to generate a series of theoretical decay curves. Curve A was calculated from half times from the relationship $t_1 = 0.69315\tau_c$. Curves B and C were calculated from fifth times and tenth times from the relationships $t_{1/5} = 0.22314\tau_c$ and $t_{1/10} = 0.10536\tau_c$ respectively. It is obvious that as the time at which the measurements are made decreases, for a specific ratio of τ_c/τ_d , the error decreases. This is intuitively satisfying, since one would expect that at zero time the electron transfer reaction would be purely charge transfer controlled, no matter what the value of τ_c/τ_d . At small ratios of τ_c/τ_d , though, the approximation is not very good even at times which are close to zero relatively. In these cases, some means must be employed to obtain the kinetic parameters other than use of the simple charge transfer approximation.

Figure 3

Determinate error in the measurement of I_0 as a function of τ_c/τ_d assuming the capacitance is known exactly, for various normalized points on the decay. (A) Half times (B) Fifth times (C) Tenth times.





Next, the errors in the determination of the capacitance using the extrapolation technique will be examined. As we have pointed out above, the extrapolation technique can involve some very large determinate errors depending on a number of factors. One of the interesting effects of using the extrapolated value of the capacitance is that it corrects to an extent the value of the exchange current calculated from the slope. The determinate errors in the estimate of the capacitance caused by mass transport processes are always in a positive direction. The slope of the log(n) vs, t curve is always less than that if the relaxation were pure charge transfer controlled. Hence, the value of ${}^{n}t=0$ is smaller than it should be and the ratio $C_d = \Delta q / n_{t=0}$ deviates in the positive direction. The values of the slope conversely deviate in the negative direction, so the product is somewhat corrected. Unfortunately, there is not a 1:1 correspondence in the change of the two variables.

Figure 4 shows the determinate error in the measure of the discharge capacitance as a function of $\log(\tau_c/\tau_d)$. The errors in this figure were calculated by taking the slopes of the $\log(\eta)$ <u>vs</u>. t curves between the points 1.00 and 2.25 of dimensionless time t/τ_d and extrapolating to zero time to find the intercept. Figure 5 shows the determinate error in the exchange

Figure 4

Determinate error in measurement of the discharge capacitance by extrapolating to zero time from the points where $t/\tau_d = 1.0$ and 2.25 as a function of τ_c/τ_d .

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Figure 5

Determinate error in the measurement of the exchange current using the simple charge transfer approximation by taking the slope of the line between the points where $t/\tau_d = 1.0$ and 2.25

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current resulting from using the extrapolated value of the capacitance and the slope for the same values of the dimensionless time corresponding to Figure 4. The errors in the capacitance become larger as R decreases, as expected, and this corrects to some extent the value of the exchange current which is calculated from the same points.

The current impulse technique provides an alternate way of measuring the capacitance. Since the form of the perturbation is a square pulse, the double layer capacitance charges linearly. From the slope of this charging curve and the magnitude of the applied current, the charge capacitance can be calculated. This measurement is also subject to some rather large errors, the origin of which become obvious if a simple model of an electrochemical cell is considered. That is. a model where the double layer capacitance is in parallel with the faradaic resistance R_r , and these are both in series with the solution resistance R_s. Phenomenologically, the presence of the faradaic reaction in parallel with the double layer capacitance consumes some of the current which is being applied to the cell, and the slope of the charging curve becomes progressively less as time proceeds. These effects become more pronounced as the faradaic resistance becomes smaller. Thus, in order for a slope measurement to be valid, an insignificant amount of the charge must have been consumed by the faradaic process up to the time of the slope measurement.

The errors in the charge capacitance can be formulated in terms of the same variables as the errors of the discharge capacitance by invoking the methodology of the galvanostatic technique (23). It will be shown in Section IV that the traditional equations derived by Delahay (28) for the galvanostatic technique can be defined in terms of τ_c and τ_d . It is sufficient for present purposes to state that this can be done and the reader is directed to Section IV-C for the details.

Figure 6 shows the error in the charge capacitance as a function of $\log(\tau_c/\tau_d)$. The errors were calculated by generating a set of dimensionless overpotential time curves with the computer, and determining the slope at the same dimensionless times t/τ_d that were used to calculate the errors in the Figures 4 and 5. A direct comparison of the errors in Figures 4 and 6 can now be made, and it can be seen that the errors in the charge capacitance are larger than the errors in the discharge capacitance, for all ratios of τ_c/τ_d . This is not surprising because in the case of the charge capacitance the system is being constantly driven by the applied current and faradaic and mass transport processes will show up sconer in time.

Figure 6

Determinate error in the measurement of the charge capacitance by taking the slope of the line between the points where $t/\tau_d = 1.0$ and 2.25.

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The computation of the exchange current with oharge capacitance gives slightly less error than the calculations with the discharge capacitance, since the capacitance values differ in the positive direction more than do the discharge values. The tabulation of the errors in the exchange current seem pointless, though, since a good measure of the capacitance as well as the exchange current is generally desired.

In view of the preceding analysis, the applicability of the simple charge transfer approximation to experimental coulostatic data is dependent on τ_c/τ_d and time. The shorter the time at which the measurements are made, the less the error. For equivalent times, the error increases as τ_c/τ_d decreases. For measurements on systems which have small ratios of τ_c/τ_d , the measurements must be made at very short time scales if the approximation is to give even a rough estimate of the reaction rate and the capacitance. The availability of the charge capacitance measurement from the current impulse technique seems to add little to the accuracy of the capacitance measurement, since this measurement is always less accurate than the discharge capacitance measurement.

C. Computer Analysis

A better approach to the problem of obtaining kinetic parameters from relaxations of the type $\tau_c \approx \tau_d$ is the technique of curve-fitting suggested by Martin (27). This is a computer based technique which involves computing a relaxation curve based on initial estimates of the capacitance and exchange current and systematically varying these two parameters to make the experimental and calculated curves fit to a predetermined degree.

Martin's original program was found to have serious limitations in the function which computed the theoretical value of the overpotential for a given set of parameters. A new program has been written and is presented as Appendix A in this thesis. The curvefitting routine has been changed from the simple Gauss-Newton method to a variation of that method by H. O. Hartly (29). This variation guarantees the convergence of the method and significantly decreases the number of iterations required to obtain convergence.

This program has been used extensively in this laboratory on several experimental systems. Figures 7, 8, and 9 indicate the kind of result which was obtained in the analysis of the hexacyanoferrate(III)/(II) couple on platinum. The experimental curves are the unbroken lines, and the crosses indicate the value of



Figure 7

Experimental and theoretical relaxation curves for the hexacyanoferrate(III)/(II) couple in 1M KCl, $C_0 = 0.01M$, $C_R = 0.01M$.

Experimental curve

x Theoretical curve calculated from curve fit values of I₀ and C_d

Data

 $C_{o} = 1.00 \times 10^{-5} \text{ moles/cm}^{3} \qquad D_{o} = 8.90 \times 10^{-6} \text{ cm}^{2}/\text{sec}$ $C_{R} = 1.00 \times 10^{-5} \text{ moles/cm}^{3} \qquad D_{R} = 7.40 \times 10^{-6} \text{ cm}^{2}/\text{sec}$ area = 0.05376 $i_{t} = 0.056 \text{ amps}$ $\tau = 1.00 \times 10^{-7} \text{ sec}$

Estimate from slope log(n) vs. tCurve fit estimate $I_0 = 0.26 \text{ amps/cm}^2$ $I_0 = 0.28 \text{ amps/cm}^2$ $C_d = 18.7 \ \mu F/cm^2$ $C_d = 18.2 \ \mu F/cm^2$





Experimental and theoretical relaxation curves for the hexacyanoferrate(III)/(II) couple in 1M KCl, $C_0 = 0.01M$, $C_R = 0.07M$.

- Experimental curve

x Theoretical curve calculated from curve fit values of I_0 and C_d

Data

$$C_{o} = 1.00 \times 10^{-5} \text{ moles/cm}^{3} \qquad D_{o} = 8.90 \times 10^{-6} \text{ cm}^{2}/\text{sec}$$

$$C_{R} = 7.00 \times 10^{-5} \text{ moles/cm}^{3} \qquad D_{R} = 7.40 \times 10^{-6} \text{ cm}^{2}/\text{sec}$$
area = 0.05376 cm² $i_{t} = 0.089 \text{ amps}$
 $\tau = 1.00 \times 10^{-7} \text{ sec}$

$$Estimate \text{ from slope } log(n) \text{ vs. t} \qquad Curve \text{ fit estimate}$$

$$I_{0} = 0.56 \text{ amps/cm}^{2} \qquad I_{0} = 0.70 \text{ amps/cm}^{2}$$

$$C_{d} = 31.3 \text{ }\mu\text{F/cm}^{2} \qquad C_{d} = 30.4 \text{ }\mu\text{ F/cm}^{2}$$



Figure 9

Experimental and theoretical relaxation curves for the hexacyanoferrate(III)/(II) couple in 1M KCl, $C_0 = 0.001M$, $C_R = 0.01M$.

--- Experimental curve

x Theoretical curve calculated from curve fit values of I₀ and C_d

Data

 $C_{o} = 1.00 \times 10^{-6} \text{ moles/cm}^{3} \qquad D_{o} = 8.90 \times 10^{-6} \text{ cm}^{2}/\text{sec}$ $C_{R} = 1.00 \times 10^{-5} \text{ moles/cm}^{3} \qquad D_{R} = 7.40 \times 10^{-6} \text{ cm}^{2}/\text{sec}$ area = 0.05376 cm² $\qquad i_{t} = 0.0613 \text{ amps}$ $\tau = 1.00 \times 10^{-7} \text{ sec}$ $Estimate from slope log(n) vs. t \qquad Curve fit estimate$ $I_{0} = 0.08 \text{ amps/cm}^{2} \qquad I_{0} = 0.058 \text{ amps/cm}^{2}$ $C_{d} = 24.9 \mu \text{ F/cm}^{2} \qquad C_{d} = 26.3 \mu \text{ F/cm}^{2}$

the overpotential, which was calculated from the final curve fit values of the exchange current and double layer capacitance. It can be seen that the system follows the simple charge transfer model over a relatively large concentration range and that the curve fit values do not differ widely from those obtained by using the simple charge transfer assumption. In this case the use of the simple charge transfer approximation is justified and it is not necessary to use the curve-fitting program to obtain estimates of the exchange current and capacitance.

The analysis of the Hg(I)/Hg system in this laboratory by Mrs. J. Kudirka proved not to be quite so straightforward. The rate of this system is quite rapid with the ratio of τ_c/τ_d ranging from about 1 to about 0.1 for the concentration ranges which were studied. There was no possibility of using the simple charge transfer assumption with any reasonable accuracy at any but the highest concentrations which were studied. Moreover, it was found at low concentrations that the simple charge transfer model did not apply to the experimental relaxation data. The relaxations decayed faster than the combination of the concentration and the diffusion coefficient mathematically allowed. It was assumed that the only way this could happen was if the concentration at the interface was larger

than the bulk concentration. In other words, it could only take place if some sort of adsorption process occurred. The program was modified to include the concentration of the Hg_2^{++} species as one of the variables to be curve fit. Many of the relaxation curves were analyzed and it was found in many cases that the curve fit value of the concentration was higher than the bulk concentration.

A typical relaxation of the Hg(I)/Hg system is shown in Figure 10. The unbroken line indicates the experimental curve, and the crosses, the relaxation curve produced by computation from the final values of the fit parameters. The values of the parameters which would have been obtained by using the simple charge transfer assumption are compared to the final curve fit values. While this approach to adsorption is hard to justify in terms of a rigorous mathematical model, the fact that relaxation curves were computed which agreed quite well with the experimental decays seems to indicate that an adsorption process is involved.

In view of this analysis of the Hg(I)/Hg system it can be concluded that the value of the rate constant reported by Weir and Enke (17) is in substantial error. The exchange currents in their study were calculated by assuming that the simple charge transfer approximation applied, and no account was taken of adsorption.



TIME #SEC



Experimental and theoretical relaxation curves for the Hg(I)/Hg system in 1M $HClO_4$, $C_0 = 0.001M$.

--- Experimental curve

o Theoretical curve calculated from curve fit values of I_0 , C_d and C_o

Data

Exactly how much the rate constant was in error is still in question. It is possible that the surface excess of the $Hg_2^{\pm\pm}$ ions was so large that it increased the ratio τ_c/τ_d to the point where the simple charge transfer approximation was justified. If this was the case, the exchange currents could be substantially correct, but the rate constant would still be in error because the concentration term used in the calculation of the rate constant would not be the bulk concentration, but rather the value of the concentration at the surface.

In all, the curve-fitting technique is capable of obtaining excellent estimates of the exchange current and the capacitance from experimental data. The uncertainty in the estimates increases as the ratio τ_c/τ_d decreases, to the limit where the observed portion of the relaxation is completely diffusion controlled, and only a lower estimate of the exchange current can be made. The chief disadvantages of the method are the amount of computer time which is required to analyze a relaxation curve, especially if τ_c/τ_d is small, and the associated problems which are inherent in the operation of any computer program of this complexity. It also is important to note that the program is always written for a particular reaction mechanism, in this case first order kinetics with no

complicating effects other than mass transport. When other effects, such as adsorption, occur, modification of the program to encompass a new model is necessary to obtain correct estimates of the rate parameters.

D. Nomographic Analysis

An alternate approach to either of the above two methods is the nomographic technique proposed by Kooijman and Sluyters (16). It is essentially a one parameter curve-fitting technique. Values of $n/n_{t=0}$ are tabulated for values of the ratio τ_c/τ_d , and the quantity $t^{\frac{1}{2}}/\tau_d^{\frac{1}{2}}$. An experimental value of $n/n_{t=0}$ is computed, and by knowing the value of the diffusional time constant and the capacitance, an estimate of the current can be calculated.

The difficulty of application of this technique is somewhere between that of curve-fitting and the simple decay analysis; consequently the accuracy of the results is also somewhere between that of the other two. The major disadvantage of this technique is that it fits only one of the two unknown parameters which control the rate of decay. A capacitance value must be assumed, and this may be very inaccurate, depending on the method and conditions under which it was obtained, as we have shown previously. Tied inextricably to the accuracy of the capacitance value is the point $n_{t=0}$ $(C_d = q/n_{t=0})$, from which the value of $n/n_{t=0}$ must be calculated. Given reasonable estimates of these parameters, the method is capable of good accuracy; however, with poor estimates the technique is only useful for getting rough values of the exchange current and correcting somewhat for the influences of mass transport.

E. Conclusion

The various ways of obtaining the capacitance and kinetic data from the coulostatic and current impulse methods have been evaluated. The best method for obtaining accurate data has been shown to be the two parameter curve-fitting technique. With this technique no prior knowledge of the capacitance or $n_{t=0}$ is necessary for the accuracy of the measurement. The experimental system need not be maximized for extremely short time measurements as long as sufficient kinetic control is evident. However, the range of the method and the ease by which it calculates the parameters are increased if these measurements are available.

The accuracy of the application of the pure charge transfer equation and the nomographic technique have been found to be dependent on accurate short time measurements. For the use of these methods the experimental system must be optimized. Within these limitations

these two techniques provide an easy way of estimating the parameters and of determining whether the curvefitting technique must be applied.

III. THE ELECTROCHEMICAL KINETICS OF THE HEXACYANOFERRATE(III)/(II) COUPLE ON PLATINUM

A. Introduction

Previous studies with the current impulse technique have been limited to just one system, the kinetics of the electrochemical reduction of the Hg(I)/Hg system (17). This reaction appeared to have some mechanistic complications, and the interpretation of some of the relaxation data proved to be somewhat anomalous. It was not clear to the investigators, in some cases, whether the complications arose from the method which was used to study the reaction, or whether the difficulties were inherent anomalies of the system. It seemed desirable for the development of the technique to show that it is capable of obtaining unambiguous data from a mechanistically simple reaction, and to extend its usefulness to the study of fast electrochemical reactions at solid electrodes. A system which fulfills these requirements is the hexacyanoferrate(III)/(II) couple on platinum. It has been the subject of much investigation, and is regarded

by many as the model of a highly reversible electrochemical reaction without complicating mechanistic effects.

The study of this couple with the current impulse technique presents several interesting problems, and gives some new data which is not available from other methods of studying fast electrochemical reactions. First, the current impulse technique gives a relatively unambiguous estimate of the differential double layer capacitance under the actual conditions of the experiment, a measurement which is not readily available from other techniques with a reaction of this rate. This ability is particularly important in this system, because the hexacyanoferrate(II) and hexacyanoferrate(III) anions are highly charged, and one might expect that the double layer capacitance of platinum would be a strong function of their concentration and the potential.

Second, these two anions are most certainly associated to a differing degree with the potassium ion of the supporting electrolyte (30), and the oxidation of the hexacyanoferrate(II) ion or the reduction of the hexacyanoferrate(III) ion probably involves a change in the number of potassium ions associated with the particular anion as it undergoes the electron transfer reaction. It would be interesting to see

whether the current impulse technique is capable of giving any information regarding this proposed mechanism.

Third, it has been reported in the literature numerous times that the rates of electrochemical reactions on platinum are very dependent on the oxidation state of the platinum surface, and more generally, on the existence of any kind of thin film on an electrode surface.

The effects of the platinum oxide film on the rate of an electrochemical reaction vary widely. Many investigators (31-33) have noted increased reversability of an electrochemical process after the electrode had been driven anodically to oxygen evolution, when presumably it was coated with an oxide film of some kind. Some of these investigators (32,33) have invoked an oxide bridging mechanism to explain this increase in reversibility. In this theory the electron transfer reaction is aided by an oxide bridge from the electrode surface to the electroactive species in the double layer. Other investigators (31) think that the entire mechanism of electron transfer reaction is changed and feel there is no need to invoke a bridging mechanism to account for the increased reactivity of the electrode. Both of these explanations appear to be valid in certain instances.

Some reactions (34-36), especially those of anions, have been found to be less reversible, and are sometimes completely supressed by the presence of an oxide film. The theory usually invoked to explain this phenomenon is an active site reduction, where the presence of an oxide film reduces the number of active sites which are available for the transfer of the electron to the electroactive species.

Needless to say, the situation concerning oxide films and their effect on the rate of electrochemical reactions is not well defined. The effects depend on how and how much the surface was oxidized, how much it was reduced, and the kind of electroactive species which was being studied. It was decided to add to the information concerning these effects by seeing what effect the presence of an oxide film had on the apparent rate constant of the hexacyanoferrate(III)/(II) couple.

B. Experimental

1) Instrumentation

One of the major experimental difficulties of the current impulse technique has been the problem of uncompensated ohmic drop during the application of the perturbing impulse. This ohmic drop, which can be many times the magnitude of the relaxation signal, tends to overdrive the amplifier system. Recovery

from this overdrive can be quite slow and can often prevent the accurate measurement of the relaxation potential for relatively long times in comparison with the pulse duration. In systems which are marginally charge transfer controlled, this is where the most meaningful kinetic information exists, so it is important to be able to make measurements in as short a time as possible.

An additional difficulty is encountered in the measurement of the charge capacitance. This measurement is made during the time of the application of the pulse and thus must be extracted from a signal which includes the ohmic drop. The elimination of the ohmic potential from the signal would allow the measurement of the charging slope at higher sensitivities and correspondingly increase the accuracy of the measurement.

A small bridge cell network has been developed in this study to minimize the IR problem, and in so doing to extend the measurement capability of the current impulse technique to shorter time scales. A diagram of the experimental system is shown in Figure 11. The compensating network is a bridge, the requirement for balance being that I_A , the current through arm A times the uncompensated solution resistance ($I_A \propto R_S$), be equal to I_B , the current through arm B times the resistance of potentiometer P_1 . The current proceeds

Figure 11

Block diagram of experimental system for compensation of ohmic drop.



from the output of the pulse generator and is split at diodes D_1 and D_2 .

Because $I_A \approx I_B$ the high speed matched diodes D_1 and D_2 turn on the two arms of the bridge simultaneously, and prevent the discharge of the double layer capacitance through the bridge network to ground when the pulse has terminated. The 100 ohm resistors insure the rapid turn-on of the diodes and serve to minimize the variation of the current in the two arms after the pulse has started. The 100 ohm precision resistor in series with the cell also served as a device to measure the magnitude of the current going to charge the double layer.

The entire circuit assembly was mounted on a grounded copper plate to isolate the various circuit components. This plate plugged directly onto the output of the pulse generator through a BNC connector. The cell was plugged through a multipin connector to the circuit.

Potentials were measured between points C and D with a sensitive differential amplifier (Tektronix P6046). This amplifier is a miniaturized probe which makes the difference measurement at the signal source, thereby eliminating the problems associated with transmitting the cell signal and compensating signal through relatively long distances to the oscilloscope. In

combination with a Tektronix 1A5 amplifier and 556 oscilloscope, the probe has a maximum sensitivity of 1 mV/cm, a risetime of 9 nsec, a bandwidth of 40 MHz, and a CMRR of 1000:1 at 40 MHz. The amplifier plugs into coaxial jacks which are mounted in the copper plate. Two sets of jacks are used, one for the current measurement and the other for the measurement of the relaxation potential.

With this system it was possible to reduce the observed IR drop to several tenths of a mV. This enhanced the ability to make an accurate charge capacitance measurement in several ways. Since the IR drop was compensated. it was possible to increase the sensitivity of the measurement to 1 mV/cm when necessary, thus increasing the accuracy of the measurement. Furthermore, since the IR drop was the same in both arms of the bridge, the small irregularities in the output of the current pulse generator cancelled in the difference signal. The system also decreased the time at which a potential measurement could be made after the start of the pulse to about 150 nsec, and decreased the time for which an accurate measurement of the relaxation potential could be made to about 100 nsec after the pulse had terminated. This is significantly better than any other system reported in the literature.

Unfortunately, this experimental system was developed after the largest part of the following study had been completed, and so a different experimental system described below was used for the majority of the reported work. It was not as good as the system ultimately developed, but was quite adequate for the studies which were performed. A block diagram of this system is shown in Figure 12.

In this system no effort was made to eliminate the IR problem. It used essentially the same instrumentation as the preceding system with the exception of the probe and IR compensating network. The perturbation source was used directly with no intervening diodes. This was possible because in its quiescent state the pulse generator had an impedance to ground which was a minimum of 10 Kohms; this was quite large with respect to the faradaic resistance of the hexacyanoferrate(III)/(II) couple. Thus the cell was essentially at open circuit after termination of the pulse, and relaxation took place only through the faradaic reaction. The Tektronix 556 oscilloscope with a 1A5 differential preamplifier was used to measure the potentials. The combination of the main frame and preamplifier had a rise time of less than 11 nsec, a 1 Mohm input resistance, and a maximum sensitivity of 1 mV/cm. The preamplifier had a

Figure 12

Block diagram of experimental system without ohmic drop compensation.


calibrated voltage which could be subtracted from the input signal. This allowed the measurement of charging curves at relatively high sensitivities by offsetting the IR drop of the cell. There was, however, an annoying irregularity in the output of the pulse generator which diminished the accuracy of the measurement to some degree. Currents were measured by inserting a calibrated 10 ohm composition resistor in series with the pulse generator and measuring the IR drop of a 1 μ sec pulse with the oscilloscope; current values were estimated to be correct to within 2 to 5%.

With both systems, experiments were initiated by an external trigger pulse which started the oscilloscope sweep. The delayed trigger output of the oscilloscope was then used to trigger the pulse generator. The experimental data were recorded photographically on Kodak Tri-X film using a Tektronix 35/C 35mm camera system. Temperature control for the activation energy studies was maintained with a Tamson TVZ-45 constant temperature bath fitted with a push-pull external circulator.

2) Cells and Electrodes

Several cell electrode systems were used in the course of this study. The one most often used, shown in Figure 13, was of small dimensions, similar to one used by Piersma, Schuldiner and Warner (37). It was

Experimental cell

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EXPERIMENTAL CELL

fitted to a small shielded box which was attached to male and female BNC connectors. The cell assembly was plugged directly onto the output of the pulse generator and a short length of BNC cable was connected from it to the input of the oscilloscope. Nitrogen was led from the purification train to the cell assembly via a small diameter Teflon tube which was immersed directly into the test solution. A second cell of slightly larger dimensions to accommodate immersion in a constant temperature bath and attachment to the IR compensating network was developed for use in the activation energy studies. Both cells demonstrated excellent high frequency response with minimal distortions due to stray inductances and capacitances.

A three electrode configuration was used in both cases, because it minimized the IR drop and gave slightly less noise than a two electrode system. The test electrode was made by melting a small diameter platinum wire with a gas-oxygen torch into a small sphere of approximately 0.05 cm² area. The geometric area of the test electrode was determined by measurement with a Bausch and Lomb microscope fitted with a micrometer eyepiece, and a calibrated micrometer slide. The area was estimated to be correct to within 2%, though no account was taken of surface roughness effects. The reference electrode was a large diameter platinum wire

of approximately 0.5 cm^2 area arranged so that it was less than 0.5 mm from the test electrode. The area of the reference was large enough so that an insignificant amount of polarization occurred at it under the conditions of the experiments. The counter-electrode was a cylinder of platinum gauze of approximately 3 cm^2 area, arranged concentrically about the reference and test electrodes.

Prior to each experiment the cell and electrodes were allowed to stand in hot perchloric acid for ten minutes. This served both to oxidize the surface of the electrodes and to oxidize any adsorbed impurities in the cell electrode system. For the reduced electrode experiments. the cell was rinsed several times with triple distilled water. filled with 1M KCL. and the electrodes were reduced for several minutes at hydrogen evolution potentials. Care was taken never to expose the electrode to the air when undergoing the changes of solution to minimize the chance that atmospheric oxygen would contaminate and oxidize the surface. For the oxidized electrode experiments, the system was used after the usual rinsing with no further treatment. The electrode surfaces produced in this way were found to be stable in their respective states for long periods of time. The system was deaerated with nitrogen for

twenty minutes before each run, though the presence of oxygen in solution was not found to affect the results significantly.

3) Reagents and Solutions

Solutions were prepared directly by weight from ACS reagent grade chemicals without further purification. Water was prepared by the redistillation of an alkaline permanganate solution of laboratory distilled water. Nitrogen used to purge solutions of oxygen was dried over calcium chloride, passed through an oven containing copper turnings at 350°C to remove traces of oxygen, passed through traps containing activated charcoal at liquid nitrogen temperatures, presaturated in a 1M KCl solution, and fed to the cell via a glass and Teflon train.

C. Experimental Results

1) Reduced Electrodes

The kinetics of the hexacyanoferrate(III)/(II) couple were measured at a total of thirteen different concentrations in 1.0M KCl. The concentration of either the hexacyanoferrate(III) or the hexacyanoferrate(II) ion was held constant at 0.01M, and the concentration of the other anion of the couple was varied in seven increments from $5 \ge 10^{-4}$ M to $7 \ge 10^{-2}$ M. The data presented subsequently is the average of at least three

separate experiments at each concentration, and in some cases is the average of as many as twenty separate experiments.

Estimates of the differential capacitance were obtained in two ways; the log(n) vs. t curves were extrapolated to zero time, to give what is known as the discharge capacitance, and in a separate experiment, a pulse of approximately 0.8 usec duration was applied to the cell and the capacitance value (denoted hereafter as the charge capacitance) was calculated directly from the slope of the charging curve. The capacitance data are presented in Figures 14 and 15 as functions of $log(C_{0})$ and $log(C_{R})$. It can be seen that there is marked agreement between the two estimates of the capacitance at all but the highest concentration, where the measured charge capacitance is significantly higher than the discharge capacitance. This apparent anomaly can be explained by considering a simple electrical model which describes the system (Figure 16). As it was discussed in Section II-B, calculation of the charge capacitance assumes that the charging process is linear with respect to time; this implies that on the time scale of the measurement (approximately one-half microsecond) an insignificant amount of the charge is used by the faradaic process, which is in parallel with the double layer capacitance. At low concentrations this

Differential capacitance from charge and discharge data of the current impulse technique, of platinum in 1M KCl as a function of $\log(Fe(CN)\frac{3}{6})$.



Differential capacitance from charge and discharge data of the current impulse technique, of platinum in 1M KCl, as a function of $\log(Fe(CN)_6^{4-})$.



Equivalent circuit of an electrochemical cell, for the case of simple charge transfer. $C_d = double layer$ capacitance, $R_s = electrolyte resistance$, $R_f = the fara-daic resistance$, and $Z_m(t) = the mass transport impedance$.



is a good approximation, and the charging curves are linear; however as the concentration increases, the exchange current increases and a significant amount of the applied current goes to the faradaic process rather than to the charging process. This causes a progressive decrease in the slope of the charging curve and leads to a high estimate of the double layer capacitance. If the slope of the charging curve could be observed at zero time, then the two estimates would presumably be the same at all concentrations; however, with the experimental system used, the minimum time for an accurate slope measurement was about 500 nsec.

In view of these considerations, it was decided that the discharge capacitance values were a better representation of the true capacitance values at the higher concentrations, since the charging time of 100 nsec for this experiment was considerably less than the 500-800 nsec required for the charging capacitance measurement. Figure 17 shows the discharge capacitance as a function of potential. This figure indicates that the differential capacitance of platinum under these conditions is essentially independent of the potential and of the concentration of the two electroactive anions, or at least that these effects cancel. The capacitance of a series of solutions with a ratio of hexacyanoferrate(III) to hexacyanoferrate(II) ion concentrations

Differential capacitance from discharge data of the current impulse technique, of platinum in 1M KCl, as a function of the measured potential <u>vs</u>. S.C.E.



of 1:1 was measured as a function of the total concentration of the two ions, from a concentration of $5 \ge 10^{-2}$ M to $3 \ge 10^{-3}$ M of each. It was found that the differential capacitance remained constant over that concentration range within experimental error. This indicates that the differential capacitance is essentially independent of the total concentration of the two anions, at least at the potential of an equimolar solution.

Exchange currents, shown in Table I, were calculated using the discharge capacitance and assuming that the observed overpotential time curves followed the simple exponential decay law dictated by pure charge transfer kinetics, $\eta = \eta_{t=0}(-t/R_fC_d)$. The use of this equation presupposes that the contributions of mass transport processes to the observed decay are minimal at the time of measurement. There are several criteria which can be applied to test this assumption, which were discussed in detail in Section II-A. One of these is that $\tau_c >> \tau_d$. At the experimental concentrations this inequality was satisfied by a factor of 25 in the most favorable case and a factor of 0.75 in the least favorable case. While it appears that the linear form of the equation is not applicable at the lower concentrations, it should be recognized that this inequality determines the condition for pure

concn $Fe(CN)_{6}^{3-}$	concn $Fe(CN)_{6}^{4-}$	Ia
mole 1. ⁻¹	mole 1. ⁻¹	amp/cm ⁻²
7.00×10^{-2}	1.00×10^{-2}	0.49
3.00×10^{-2}	1.00×10^{-2}	0.32
1.00×10^{-2}	1.00×10^{-2}	0.23
7.00×10^{-3}	1.00×10^{-2}	0.19
3.00×10^{-3}	1.00×10^{-2}	0.11
1.00×10^{-3}	1.00×10^{-2}	0.079
5.00 x 10^{-4}	1.00×10^{-2}	0.050
1.00×10^{-2}	7.00 x 10^{-2}	0.62
1.00×10^{-2}	3.00×10^{-2}	0.38
1.00×10^{-2}	7.00×10^{-3}	0.20
1.00×10^{-2}	3.00×10^{-3}	0.12
1.00×10^{-2}	1.00×10^{-3}	0.093
1.00×10^{-2}	5.00×10^{-4}	0.052

Values of the Apparent Exchange Current Density for Solutions of Varying Concentrations of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ in 1.00M KC1 at 25°³

TABLE I

charge transfer control throughout the entire relaxation time, as has been discussed in Section II-B. Even at the low concentrations, though, the decay is charge transfer controlled at short times. Special care was taken at the low concentrations to use initial slopes in the calculation of the exchange current and to obtain good estimates of the capacitance, so that the determinate error due to negligence of mass transport processes was minimized.

Some of the experimental data was analyzed with the computer program of Appendix A. Some of the results are presented in Section II-C and additional results are presented here in Figures 18 and 19. The values of the curve fit parameters are compared with the values obtained using the simple charge transfer approximation. It can be seen that both approaches give essentially the same results. The average obtained from both methods for a number of data points was found to be essentially the same. Thus, it was felt that the use of the simple charge transfer assumption to calculate the exchange currents was justified. The calculated and experimental curves of Figures 18 and 19 fit very well, indicating that the electrode reaction is a simple first order electron process.



Figure 18

Experimental and theoretical relaxation curves for the hexacyanoferrate(III)/(II) couple in 1M KCl, $C_0 = 0.003M$, $C_R = 0.001M$.

- Experimental decay curve

x Theoretical decay curve

Data



Experimental and theoretical relaxation curves for the hexacyanoferrate(III)/(II) couple in 1M KCl, $C_0 = 0.01M$, $C_p = 0.01M$.

Experimental decay curve

x Theoretical decay curve

Data

The reaction-order plots shown in Figures 20 and 21 were made using the exchange currents in Table I and the measured concentration. The plots are linear over the entire concentration range and give transfer coefficients (α) of 0.54 and 0.46 respectively. No significance should be attached to the observed differences in the transfer coefficient since these deviations are within experimental error. The heterogeneous rate constant $k_s (I_0 = nFAk_s C_R^{\alpha} C_0^{1-\alpha})$ calculated from the average of the exchange currents at a concentration of 0.01M in each ion was found to be 0.24 cm/sec. The exchange current of a 0.01M solution in each ion was measured at ten degrees. thirty degrees, and fifty degrees. $Log(I_0)$ was plotted as a function of 1/T, and an activation energy of 3.1 ± 0.2 kcal/mole was calculated.

2) Oxidized Electrodes

The work completed on oxidized electrodes must be considered of a preliminary nature because of some rather persistent discrepancies which were very difficult to explain. The oxidized electrodes which were studied were produced by oxidation of the platinum electrode with hot perchloric acid. Though this oxidation procedure is extreme, it produced an electrode surface

Reaction-order plot for the hexacyanoferrate(III)/(II) couple on platinum in 1M KCl, $C_0 = 0.01M$.



Reaction-order plot for the hexacyanoferrate(III)/(II) couple on platinum in 1M KCl, $C_{R} = 0.01M$.

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state which was fairly reproducible for kinetic measurements.

The number of measurements and variety of solutions which were studied were not as numerous as those in the reduced electrode experiments, but were sufficient to establish several facts. The first of these is that the apparent rate of exchange at perchloric acid oxidized electrodes is drastically reduced from that measured for reduced electrodes at equivalent experimental conditions.

The second is that the morphology of the experimental overpotential time curves was not consistent with the model which describes simple charge transfer processes. With the apparent reduction of the rate of charge transfer of ten, the inequality $\tau_c > \tau_d$, which determines whether the decay is charge transfer controlled, is satisfied to the extent that the log(n) vs. t curve should be virtually linear at the measured times. However this behavior was consistently not observed. The log(n) vs. t curves deviated at long times in ways that suggested the decay was partially mass transport controlled. These essential facts are illustrated in Figure 22. The experimental curve is designated by crosses and the theoretical decay calculated from the experimentally determined parameters is shown as the unbroken line. It can be seen

Experimental and theoretical relaxation curves for the hexacyanoferrate(III)/(II) couple in 1M KCl, $C_0 = 0.01M$, $C_R = 0.01M$, oxidized electrode.

- x Experimental decay
- Theoretical decay for experimentally determined values of I₀ and C_d

Data



that there is substantial deviation of the experimental curve from the theoretical decay at long times.

The third discrepancy is the fact that the measured value of the capacitance was consistently lower for the oxidized electrodes than it was for the reduced electrodes. Though the capacitance values were fairly scattered, the average value for the capacitance of an oxidized electrode at a concentration of 10^{-2} M in both the hexacyanoferrate(III) and hexacyanoferrate(II) ions was 11 μ F/cm². This is about 40% of the measured value of 25 μ F/cm² for reduced electrodes at the same concentration. Most other investigators (38,39) have Feported increased values of the capacitance upon Oxidation of the platinum surface.

Several approaches to the explanation of these Experimental anomalies have been attempted. The most fruitful of these, which is not without its theoretical limitations, is to consider a reduction in the effective area of the electrode due to blockage by the platinum Oxide of the "active sites" where electron transfer takes place. If the geometric area of the electrode is taken as A, and the fraction of the surface covered by oxide is taken as ϕ , the electrode area available for electron transfer is $A^* = A_{\phi}$.

Some of the oxidized electrode decays were mathematically analyzed by invoking this area mechanism

using a simple modification of the program in Appendix A. The capacitance and exchange current were changed proportionately (thus the $R_{f}C_{d}$ time constant remained the same but the increased exchange current allowed diffusion processes to appear) by decreasing the effective area. The results of one of these computations is shown in Figure 23. When the effective area was reduced from the geometric area of 0.0835 cm^2 to 0.0152 cm^2 the experimental and theoretical curves fit quite well. The final values of the capacitance and exchange current which were obtained are 55 μ F/cm² and 0.184 amps/cm² for the effective area. Thus it appears that estimate of the rate constant obtained at oxidized electrodes by considering the measured exchange current and the geometric area gives a value which is much too small.

It is easy to rationalize the effects that platinum oxide might have on the exchange current by considering the way in which these films were formed. Boiling perchloric acid is a very good oxidizer and it is not hard to imagine multiple oxide layers on various parts of the electrode. The sites on the electrode surface which are active to electron transfer may be the places where oxide films form preferentially. There may be several layers of oxide built up at these sites and thus electron transfer may not take place

Experimental and theoretical relaxation curves for the hexacyanoferrate(III)/(II) couple in 1M KCl, $C_0 = 0.01M$, $C_R = 0.01M$, oxidized electrode.

- x Experimental decay
- ---- Theoretical decay for experimentally determined values of I_0 and C_d
- Theoretical decay calculated by invoking area mechanism

Data

 $C_{o} = 1.00 \times 10^{-5} \text{ moles/cm}^{3} \qquad D_{o} = 8.90 \times 10^{-6} \text{ cm}^{2}/\text{sec}$ $C_{R} = 1.00 \times 10^{-5} \text{ moles/cm}^{3} \qquad D_{R} = 7.40 \times 10^{-6} \text{ cm}^{2}/\text{sec}$ area = 0.0835 cm² $i_{t} = 0.0368 \text{ amps}$ $\tau = 1.00 \times 10^{-7} \text{ sec}$ $\frac{\text{Parameters determined by invoking area mechanism}}{I_{0} = 0.184 \text{ amps/cm}^{2}}$ $C_{d} = 55 \text{ } \mu\text{F/cm}^{2}$



at these places as readily as across other parts of the electrode surface. The sites which are not oxidized to this extent may present a lower energy barrier to electron transfer and thus determine the rate of decay. This does not exclude the possibility that several rate processes occur at the surface, one of which is much faster than the other.

It is not so easy to explain why the measured value of the capacitance is lower than the value of 50 $_{\rm u}$ F/cm² reported by other investigators. The answer to this may also lie in the extreme procedure used to make the oxidized surface. Other investigators (38,39) have made their oxidized surfaces with relatively mild electrochemical oxidizing techniques. These mild techniques produce a surface which is essentially a monolayer of oxide coating. The multiple layers which were probably formed with the present procedure on select sites of the electrode would account for the low value of the measured capacitance. The capacitance at these sites would be much lower than at other parts of the electrode and would dominate the measured value of the capacitance.

It is not clear whether the apparent value of the capacitance obtained by reducing the effective area has any significance other than a mathematical one. It is the capacitance which was mathematically

necessary to make the experimental and theoretical curves fit by reducing the area. The similarity between the "effective" area value of 55 μ F/cm² and the value of 50 μ F/cm² obtained by other investigators for oxidized electrodes for total area should not be construed to mean that the two surfaces were the same. The similarity of the two values may have no physical meaning.

Figure 24 is a reaction order plot which shows the exchange current per electrode as a function of $log(C_0)$, $C_p = 10^{-2}$ M. The slope is dependent only on the change in exchange current with concentration and is independent of the area. all other things being constant. The measured value of the transfer coefficient is 0.46, which is substantially the same as that obtained for reduced electrodes. A rate constant of 0.028 was calculated, based on the geometric area and the average exchange current of a number of experiments of a 0.01M hexacyanoferrate(II), 0.01M hexacyanoferrate(III) solution at 30°C. The activation energy was also determined by obtaining the exchange current of 0.01M hexacyanoferrate(II), 0.01M hexacyanoferrate(III) solution at three temperatures and was found to be 3.5 + 0.5 kcal/mole. The activation energy is also independent of the area, depending only on the change of the exchange current with T. This

Reaction-order plot for the hexacyanoferrate(III)/(II) couple on platinum in 1M KCl, $C_{\rm R} = 0.01$ M, oxidized electrode.


also agrees reasonably well with the value obtained with reduced electrodes.

The above evidence, while by no means conclusive, seems to suggest that the essential rate process is the same at oxidized and reduced electrodes. However, it is not really possible to postulate the mechanism by which surface oxidation affects the reaction rate without further rate studies on a variety of carefully controlled surface oxidation states.

3) Mechanistic Conclusions

Nothing in the present investigation suggests that the rate of this reaction is affected by anything other than surface oxidation. It appears to be a first order electron transfer reaction with no complicating kinetic steps. The linearity of the reaction order plot over the entire concentration range, the independence of the differential capacitance with respect to either the applied current or the potential, and the marked agreement between the charge and discharge capacitance at all but the highest concentrations all support this conclusion. One could propose a mechanism based upon the association constants measured by Eaton, George, and Hanania (30) of

 $(K_n Fe(CN)_6)^{n-3} + K^+ + e^- \stackrel{>}{\leftarrow} (K_{n+1} Fe(CN)_6)^{n-3}$ but if such steps take place, the current impulse technique gives no information to prove or disprove

them. The association-dissociation reaction is probably extremely rapid with respect to the electron transfer reaction.

4) Comparison of Results

A comparison of the results of the present investigation with those of previous investigators is presented in Table II. It can be seen that the current impulse technique gives a rate constant for reduced electrodes which is about twice as large as that measured by any of the other techniques, while that measured for oxidized electrodes is substantially less than any of the others. The estimates of apparent transfer coefficient agree very well except for the value obtained by Jahn and Vielstich (42) with the rotating disc electrode. It is concluded that the observed differences in the rate constants are primarily due to differences in electrode conditioning. It has been shown that the apparent rate constant is dependent on the amount of surface oxidation, though the measurement of the transfer coefficient is not. The conditioning procedures reported by previous investigators promote varying amounts of surface oxidation as has been verified in this laboratory, so their results are bound to be lower than the ones of the present investigation.

TABLE II

Comparison of Present Kinetic Results with Results of Previous Investigators^a

Investigator(s)	Technique	Ref.	Apparent Transfer Coeff.	Std. Rate Const. cm/sec-1	
Randles and Somerton	Faradaic impedance	40		0.09	
Jordan	Hydrodynamic voltammetry	41		0.08	
Jahn and Vielstich	Rotating disc electrode	42	0.61	0.05 (C)	
Agarwal	Faradaic rectification	43	0.49		
Wijnen and Smit	Cyclic potential step	44	0.55	0.095 (C)	
Wijnen and Smit	Cyclic coulombic step	44	0.50	0.13 (C)	
Daum and Enke	Current impulse reduced electrode		0.50 (avg.)	0.24	
Daum and Enke	Current impulse oxidized electrode		0.46	0.028	

^aResults designated (C) were not reported by the respective authors but are calculated from their data.

IV. A NEW APPROACH TO

GALVANOSTATIC MEASUREMENTS

A. Introduction

An alternate method for the study of fast electrochemical processes is the galvanostatic technique. It is subject to many of the same problems as the coulostatic and current impulse techniques and these problems can be formulated in much the same way, since the characteristic parameters, τ_c and τ_d , which characterize these methods are the same.

The galvanostatic technique is very simple conceptually. A constant current of precise magnitude is applied to an electrochemical cell and the potential is followed as a function of time. The perturbation is limited in magnitude by the requirement of linearization of the absolute rate equation to a few millivolts anodic or cathodic of the equilibrium potential.

Initially, upon application of the current, the test electrode will depart from its equilibrium value towards the charge transfer overpotential n_c , which is the potential which allows the electrochemical reaction to proceed at a rate and in a direction which

is consistent with the current which is being applied and the concentrations of the reactants in the bulk of the solution. It is prevented from reaching this potential instantaneously by the existence of the double layer capacitance which is in parallel with the faradaic process. The charging of the capacitance consumes a significant amount of the applied current initially $(i_t = C_d dn/dt)$, so that not all of the applied current is being consumed by the faradaic process. After the initial charging process, the rate of potential change with time decreases drastically, and essentially all of the current goes to the faradaic process. As time proceeds thereafter. the electrode reaction. if it is of sufficient rate. depletes the concentration of reactant and increases the concentration of product at the electrode surface, and causes the appearance of the mass transport or diffusion overpotential and this gradually increases as time proceeds.

Berzins and Delahay (23) simultaneously with Lorenz (45) derived Equation 1, which describes the processes which occurred at the electrode:

$$\eta = \frac{RTi}{nF} t \left[\frac{1}{nF} C^{0}k_{s} + 2\left(\frac{t}{\pi}\right)^{1/2} nFC^{0}\left(\frac{1}{D_{0}^{1/2}} + \frac{1}{D_{R}^{1/2}}\right) \right]$$
(1)

where $C^{O} = C_{O} = C_{R}$. Initially they considered only the processes of diffusion and charge transfer. It was thought that the charging of the double layer took

place in less than a μ sec, and thereafter changes in the morphology of the n <u>vs</u>. t curve due to further charging of the double layer were not important. The equation which they derived shows a square root dependence of the potential on time, with the intercept being proportional to the faradaic resistance.

The concept of the method was to extrapolate the part of the curve which was diffusion controlled and followed square root time dependence to zero time, where presumably the process was purely charge transfer controlled and thus obtain the charge transfer overpotential from which the exchange current could be calculated.

It was determined later that the charging of the double layer affected the morphology of the n <u>vs</u>. t curve at times longer than those originally considered. Berzins and Delahay (28) reconsidered the problem including both charging and mass transport processes, and derived the following equations:

$$n = \frac{1_{t}}{C_{d}(\gamma-\beta)} \{ \frac{\gamma}{\beta^{2}} [\exp(\beta^{2}t) \operatorname{erfc}(\beta t^{1/2}) + 2\beta(\frac{t}{\pi})^{1/2} - 1] - \frac{\beta}{\gamma^{2}} [\exp(\gamma^{2}t) \operatorname{erfc}(\gamma t^{1/2}) + 2\gamma(\frac{t}{\pi})^{1/2} - 1] \}$$
(2)

$$\beta_{,\gamma} = \frac{I}{2nF} \left(\frac{1}{C_{o}^{\prime}D_{o}} + \frac{1}{C_{R}^{\prime}D_{R}} \right) \pm \left[\frac{I}{4n^{2}F^{2}} \left(\frac{1}{C_{o}^{\prime}D_{o}} + \frac{1}{C_{R}^{\prime}D_{R}} \right)^{2} - \frac{nFI}{RTC_{d}} \right]^{2}.$$
(3)

This equation was then linearized by eliminating the $exp(X^2)erfc(X)$ terms by assuming those terms were negligible when t was greater than 50 microseconds.

The linearized form, Equation 4, is essentially the same as that originally derived by Delahay, with the exception of the term containing C_d , which is the correction term for double layer charging.

$$\eta = \frac{-RTi}{nF} t \left\{ \frac{2}{\sqrt{\pi}nF} \left(\frac{1}{C_{0}\sqrt{D_{0}}} + \frac{1}{C_{R}\sqrt{D_{R}}} \right) t - \frac{RTC_{d}}{nF} \left[\frac{1}{nF} \left(\frac{1}{C_{0}\sqrt{D_{0}}} + \frac{1}{C_{R}\sqrt{D_{R}}} \right) \right]^{2} - \frac{1}{I_{0}} \right\}$$
(4)

There are several problems both experimental and theoretical which impair the general usefulness and mar the essential simplicity of the galvanostatic technique. These problems are especially acute when studying very rapid reactions. As k_s increases, larger currents must be applied to the test electrode to obtain a measureable charge transfer overvoltage. Measurements must therefore be made at short times to keep the mass transfer overvoltage comparable to the charge transfer overvoltage. Consequently the contribution of charging processes and ill-defined mass transport process to the morphology of the n <u>vs</u>. t curve become increasingly large, and nonlinearity of the n <u>vs</u>. $t^{\frac{1}{2}}$ curves become evident.

An experimental approach to this problem proposed by Gerischer and Krause (24) and used by many investigators was the double pulse galvanostatic method. With this method a pre-pulse of constant current of very short duration and high magnitude was applied to the cell to pre-charge the double layer to some

potential close to the charge transfer overpotential. In this way all of the current of the second pulse would be consumed by the faradaic process and not by the charging process. Experimentally the magnitude of the pre-pulse was adjusted so that the overpotential time curve started with a horizontal tangent at the beginning of the second pulse; thus the current passing through the cell would be entirely faradaic at that instant.

Kooijman and Sluyters (25) have recently considered the experimental difficulties incurred in adjusting the magnitude of the pre-pulse so that the initial cell response to the application of the constant current is a horizontal tangent. They have concluded that with present-day equipment the double pulse technique has little to offer over the conventional galvanostatic technique. They conclude that the maximum rate constant which can be studied is 0.5 cm/sec.

Several mathematical methods have been developed to obtain charge transfer parameters from very fast systems. The first of these attempts was by Birke and Roe (46) in their study of the highly reversable Hg(I)/Hg system. Birke and Roe observed nonlinearity in their $n vs. t^{\frac{1}{2}}$ plots at short times, and after a detailed examination of the mathematics, concluded that the nonlinearity was due to the neglect of the

 $\exp(X^2)\operatorname{erfc}(X)$ terms in Delahay's equation. They then proceeded to expand the $\exp(X^2)\operatorname{erfc}(X)$ terms in a Maclaurin series and included the first few terms in the equation which they used. They calculated their exchange currents by an iterative procedure, the first estimate being that of the $n \underline{vs}$. $t^{\frac{1}{2}}$ intercept. Unfortunately, after doing all of this work, they concluded that the curvature was due to other causes and proceeded to do the major portion of the work with the double pulse galvanostatic technique (47).

Kooijman and Sluyters (16) proposed an alternate mathematical solution to this problem. They calculated values of the dimensionless overpotential as a function of $at^{\frac{1}{2}}$ for a variety of values of $(\beta+\gamma)^2/\beta\gamma$, where $a = n^2 F^2/RTC_d (1/C_0 D_0^{\frac{1}{2}} + 1/C_R D_R^{\frac{1}{2}})$. The exchange current is calculated assuming the knowledge of t, C_0 , C_R , D_0 , D_R , C_d and i_t , computing a value of $at^{\frac{1}{2}}$ and the dimensionless overpotential, and reading the value of $(\beta+\gamma)^2/\beta\gamma$. From the value of this ratio the exchange current can be calculated. This can be done for several points to assure the validity of the model which is used, and to obtain an average value of the exchange.

The major disadvantage of the technique is the necessity of assuming a capacitance value for the system. The values which are usually used are those obtained

by some other technique, generally under nonreactive conditions. These values are not necessarily correct, for there is no <u>a priori</u> reason to believe that the capacitance value obtained under other experimental conditions will be the same as those of the system under highly reactive conditions for which the above corrections are necessary. In fact there is frequently good reason to believe that the capacitance values may be quite different. With solid electrodes there is no good reason to assume a capacitance value at any time, since those measurements are dependent on the time of day at which they are taken and are rarely reproducible to the required precision.

The second problem is that of uncompensated solution resistance. As has been mentioned, with fast reactions it is necessary to use high applied currents in order to obtain a measureable charge transfer overpotential. The uncompensated solution resistance may cause an ohmic drop which may be many times the magnitude of the overpotential of the system. This must be either known and subtracted from the total signal, or compensated with an electronic circuit. Any uncertainty in the value of the ohmic drop directly affects the estimate of the charge transfer overpotential. For very rapid reactions the extrapolated value of the charge transfer overpotential is almost

always less than a millivolt, so the IR drop must be known to less than a tenth of a millivolt in order to obtain measurements of the exchange current which are accurate to 10%.

These effects have been pointed out by many authors and several means have been developed to eliminate the problem experimentally and mathematically (48-50). Most of the experimental systems have been simple variations of the original bridge circuit proposed by Berzins and Delahay (28). The problem has always been to find a differential amplifier with a sensitivity of at least 1 mV/cm, which has a high bandpass (greater than 10 MHz) and an extremely high common mode rejection ratio, so that the overvoltage can be accurately extracted from a signal many times its magnitude. Coupled with the IR problem is the problem of the definition of zero time. For extremely rapid reactions it is necessary to define zero time very accurately, and this is often not possible because of noise and initial mismatch of the IR compensator.

Finally, but by no means the least of the problems, are the conditions for which the simplified form of the exact equation derived by Berzins and Delahay (28) is applicable. Reduction of the exact equation requires that the terms containing the $\exp(X^2)\operatorname{erfc}(X)$ be very small with respect to the other terms in the

equation. The situation where these terms are negligible is somewhat clouded, since for most reasonable values of the parameters for an electrochemical system these arguments are complex. Berzins and Delahay (28) arrived at a general time condition of t >> 50 µsec by considering sets of electrochemical parameters where the arguments of these functions are real. Obviously this condition is not of general applicability and later Inman, Bokris and Blomgren (48) emphasized that the condition t $>> 50/\beta^2$ should be used in its place.

The entire problem of linearization was reconsidered in detail by Kooijman and Sluyters (51). They derived a generalized time condition of

$$t > 100 \left| \frac{(\beta + \gamma)^2 - 2\beta\gamma}{2\beta^2\gamma^2} \right|$$
 (5)

for which Equation 4 holds to 1%. They showed that this reduces to somewhat simpler forms when three general cases were considered:

$$(\beta_{+\gamma})^2 << \beta_{\gamma}, t > 100/\beta_{\gamma}$$
 (5a)

$$(\beta_{+\gamma})^2 >> \beta_{\gamma}, t > 50(\beta_{+\gamma})^2/\beta^2\gamma^2$$
 (5b)

$$(\beta_{+}\gamma)^{2} \simeq 2 \beta_{\gamma}, t > 5/\beta_{\gamma}$$
 (5c)

B. Scope of Reported Research

The mathematical formalism of the galvanostatic technique will be reformulated in terms of the charge transfer time constant and diffusional time constant τ_c and τ_d , which are equivalent to those in the coulostatic technique. While this transformation is trivial mathematically, it allows the problems of the technique to attain a physical significance which is not immediately evident from the traditional formalism.

The conditions for the reduction of Equation 2 to Equation 4 will be reexamined in terms of the ratio τ_c/τ_d and $t^{\frac{1}{2}}/\tau_d^{\frac{1}{2}}$, and the consequences of the errors involved in assuming the linear equation are discussed. Finally an approach will be suggested for the study of rapid electrochemical reactions and some preliminary experimental data on the hexacyanoferrate(III)/(II) couple will be presented.

C. Theory

We can define a charge transfer time constant

$$\tau_{c} = RT/nFI_{0} \tag{6}$$

and a diffusional time constant

$$d = [(RTC_d/n^2F^2)(1/C_0D_0^{\frac{1}{2}} + 1/C_RD_R^{\frac{1}{2}})]_1^2$$

just as we did in the coulostatic technique. Then β , γ of Equation 3 become

$$\beta_{\bullet} \gamma = \tau_{d}^{\frac{1}{2}} \pm [(\tau_{d}^{\frac{1}{2}} - 4)/4\tau_{c}]^{\frac{1}{2}}.$$
 (8)

Equation 4, which is the reduced form of Equation 2, transforms to

$$n = (\mathbf{1}_{t} / \mathbf{C}_{d}) (\tau_{d}^{\frac{1}{2}} (t / \pi)^{\frac{1}{2}} + \tau_{c}^{-\tau_{d}}$$
(9)

and the intercept of this equation at zero time is

$$n_{o} = (i_{t}/C_{d})(\tau_{c} - \tau_{d})$$
(10)

Some of the difficulties in obtaining estimates of the heterogeneous rate constant and exchange currents of fast reactions can now be discussed in terms of these variables. The ratio τ_c/τ_d can be considered an indicator of the measureability of the charge transfer parameters of an electrochemical reaction. When this ratio is large, the amount of kinetic information is large, since perturbations due to mass transport are small with relation to the charge transfer process. As the ratio becomes smaller, the amount of kinetic information becomes smaller because mass transport dominates the η vs. t morphology. In the galvanostatic technique the amount of information on the charge transfer process with relation to other types of information is proportional to the intercept.

The galvanostatic technique is limited to small overvoltages because of the requirement of linearization of the absolute rate equation. The technique has also been historically limited by the assumption of Equation 4 for the calculation of the intercept, and hence the charge transfer resistance, and this equation is only valid for long times.

The ratio of the intercept at time zero to the overpotential at time t where the reduced equation is

applicable is $\tau_d^{\frac{1}{2}}(t/\pi)^{\frac{1}{2}}/\tau_c^{-\tau}d$. It can be easily seen that as τ_d and time increase, the intercept becomes a smaller fraction of the potential at time t and that part of the intercept which relates to charge transfer becomes a smaller fraction of the intercept.

It would seem that the ratio could be made more favorable by increasing the applied current and reducing the time at which the measurements are made, so that the signal to noise ratio can be made more favorable. However this has not been done, because Equation 4 is not applicable at short times.

Figure 25 shows an analysis of the errors involved in the determination of the exchange current as a function of the ratio τ_d/τ_c to indicate the time ranges for which the assumption of the linear equation is valid. The errors were calculated by generating a series of tables of the dimensionless overpotential $n^* = nC_d/\tau_d i_t$, and dimensionless square root time $t^{\frac{1}{2}}/\tau_d^{\frac{1}{2}}$ for ratios of τ_d/τ_c from 0.01 to 10.0 with a modified version of the program in Appendix B. The only region where the error approaches zero is the point where $\tau_d/\tau_c \approx 2$, no matter from what time the extrapolation is made. This is in apparent disagreement with the criterion developed by other investigators for the assumption of the validity of the reduced equation.

Figure 25

Determinate error incurred in measurement of exchange current in the galvanostatic technique by using Equation IV-4.

Α.	From	the	points	where	$t^{\frac{1}{2}}/\tau^{\frac{1}{2}}_{d}$	=	10.0	and	9.0
з.	From	the	points	where	t ¹ / d	=	22.0	and	20.0
с.	From	the	points	where	$t^{\frac{1}{2}}/t^{\frac{1}{2}}$	Ξ	45.0	and	40.0



The criterion which other investigators have used is that the reduced Equation 4 agree with the general Equation 2 to within 1 %. However, this is not sufficient guarantee that the intercept, hence the value of the exchange current, will be accurate to 1%. For example, consider Kooijman and Sluyters' (51) second case, and the time condition which they derive, <u>i.e.</u>, for $(\beta_{+\gamma})^2/\beta_{\gamma}$ or in present notation $\tau_d/\tau_c >> 1$, $t > 50(\beta_{+\gamma})^2/\beta_{\gamma}^2/r^2$.

Consider a system with the following parameters, $D_o = D_R = 10^{-5} \text{ cm}^2/\text{sec}$, $C_o = C_R = 10^{-6} \text{ moles/cm}^3$, $C_d = 2.0 \times 10^{-5} \text{ F/cm}^2$, $I_0 = 0.4501 \text{ amps/cm}^2$, n = 1, $T = 300^{\circ}$ K. The ratio τ_d/τ_c for the system will be 10.

According to Kooijman and Sluyters (51) the condition for the application of Equation 4 is that $t = 5.743 \times 10^{-4}$ sec. Taking the dimensionless time points of $t^{\frac{1}{2}}/\tau_d^{\frac{1}{2}} = 10$ and 12, one calculates that the times are 1.149×10^{-3} and 1.65×10^{-3} sec respectively, which certainly satisfy the above requirement. The values of the dimensionless overpotential calculated from the exact equation are 10.4288 and 12.6781 respectively. Using the reduced equation, values of 10.3838 and 12.6405 are calculated, and these are within 1%. However, the intercept is equal to -0.32, which is about 3% of the total value of the overpotential and gives an error in the value of the exchange current of about 40%. Thus the requirement that Equation 4 be within 1% of Equation 2 is not sufficient guarantee that the measurement will be accurate.

Little is to be gained from extending the experiment to longer times where the two equations agree better. For if the value of the overpotential at the above times is about 5 mV, then the intercept will be about -0.15 mV, which is a very marginal signal. The longer the time, with the limitation that n < 5 mV, the smaller the intercept, and it ultimately becomes immeasureable.

D. A New Approach to

Galvanostatic Measurements

A new approach to galvanostatic measurements is proposed here which makes no assumptions about either the validity of the reduced equation or the value of the double layer capacitance. The experimental approach is of different emphasis than that traditionally used by experimenters in that extremely high currents are applied to the test electrode to make the charge transfer overvoltage a significant portion of the magnitude of the allowed overpotential. This requires that measurements be made at very short times to insure the 5 mV limit is not exceeded and to allow an experimental estimate of the value of the double layer capacitance.

The data is analyzed by curve fitting the experimantal overpotential time curve with a computer program which calculates the theoretical overvoltage for a given set of experimental parameters. The same curve fitting routine which was used for the current impulse technique is used in the galvanostatic technique to manipulate the experimental data to obtain estimates of the exchange current and capacitance.

This experimental approach has been made possible by the availability of some new instrumentation which enables the experimenter to apply relatively high currents to the electrochemical cell and still extract the overpotential from a signal which includes a very large ohmic drop.

1) Experimental

Some very preliminary galvanostatic measurements have been made on the hexacyanoferrate(III)/(II) system. This system does not fulfill the requirements necessary really to test the validity of this approach to galvanostatic measurements for fast systems. Though the rate constant of 0.28 cm/sec is moderately high, the applicability of this method would show its real advantages in systems where the heterogenous rate constant is 1 cm/sec and higher. Measurements were made in systems where the concentration of the hexacyanoferrate(III)/(II) was high in order to insure large exchange currents,

but the ratio of τ_c/τ_d was so large that it was quite easy to do the measurements in the conventional way.

The instrumentation was essentially the same as that described in Section III-B-1. The combination Tektronix 556 oscilloscope, P6046 probe and PG-32 pulse generator were used without significant modification. The IR compensating circuit was modified by the addition of a 1000 ohm resistor in series with the output of the pulse generator to limit the currents to values which were consistent with the reaction which was studied. With this experimental system it was possible to make measurements from times as short as 100 nanoseconds after the start of the current pulse and IR compensation was good to at least 0.1 mV.

The procedure including chemicals, electrode preparation and so forth, was exactly the same as that described in Section II-B for reduced platinum electrodes.

2) Results and Conclusions

The experimental results were quite varied, and correspondingly quite inconclusive. A typical galvanostat of the hexacyanoferrate(III)/(II) couple is shown in Figure 26, along with the curve fit parameters of the exchange current and capacitance. Results at any one concentration varied by as much as 100% above and below the average value obtained with the current

Figure 26

Experimental and theoretical relaxation curves for the hexacyanoferrate(III)/(II) couple in 1M KCl, $C_0 = 0.03M$, $C_p = 0.01M$.

- Experimental curve

x Theoretical curve calculated from curve fit values of I_0 and C_d

Data



ηmV

impulse technique under the same experimental conditions. The morphology of the n <u>vs</u>. t curve was dependent on the position of the test electrode with respect to the counter and reference electrodes, among other things. Results could vary up to 50% on the same experimental solution just by varying the position of the test electrode with respect to the reference several millimeters. This kind of result points out the difficulties which experimenters encounter when trying to make kinetic measurements during a perturbation. The problems of noise, cell geometry, shielding, and frequency dispersion are all magnified under these conditions.

Although these results are inconclusive, there is no reason, in principle, why the method will not work. The disparity of the above results is undoubtedly due to some experimental problem which will take some time and ingenuity to work out. The method holds great promise for the examination of extremely fast reactions with the galvanostatic method without resorting to the usual compromises in either the experimental or mathematical parts of the technique.

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APPENDICES

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APPENDIX A

PROGRAMS FOR NUMERICAL CALCULATIONS ON COULOSTATIC DATA

A. Equations for Calculation of

Overpotential Time Curves

The mathematics of the theoretical coulostatic equation (Equation II-1) including mass transport are simple when the quantity $\tau_d/4\tau_c$ is greater than one. The exp(X²)erfc(X) are real, and several well-known asymtotic expansions are available to calculate the values of these functions. When $\tau_d/4\tau_c$ is less than one the arguments of these functions become complex and the calculations become more difficult.

In these cases the error function complement can be expressed by

$$erfc(-iz) = 1 + \frac{2i}{\sqrt{\pi}} \int_{0}^{z} exp(t^{2})dt$$
 (1)

where in general $z = x \pm iy$. The function

$$W(z) = \exp(-z^2) \operatorname{erfc}(iz)$$
 (2)

has also been defined and can be expressed as

$$W(z) = \exp(-z^2) \left[1 + \frac{21}{\sqrt{\pi}} \int_{0}^{z} \exp(t^2) dt\right]$$
 (3)

and this function can be evaluated on the basis of an infinite series expansion,

$$W(z) = \sum_{n=0}^{\infty} \frac{(1z)^n}{\Gamma(\frac{n}{2}+1)}$$
(4)

where $\Gamma(\mathbf{r})$ is the Gamma function of r. The function we really desire is

$$exp(z^2)erfc(z)$$
 (5)

and we can obtain this by substituting the quantity (iz) for (z) in the above equations. The resulting equation is then

$$W(1z) = \exp(z^{2})\operatorname{erfc}(z) = \sum_{n=0}^{\infty} \frac{(-1)^{n}(z)^{n}}{\Gamma(\frac{n}{2}+1)} .$$
(6)

This equation suffices for small values of the arguments x and y. For large values of these arguments, however, it is more convenient to use the following asymptotic expansion:

$$\exp(z^{2})\operatorname{erfc}(z) = \frac{1}{\sqrt{\pi}z} \{1 + \sum_{m=1}^{\infty} (-1)^{m} \frac{1 \cdot 3 \cdot 5 \cdot \cdot \cdot (2m-1)}{(2z^{2})^{m}}, (7)\}$$

These equations were used to write a FUNCTION PROGRAM in FORTRAN IV for the calculation of the theoretical value of the overpotential for given values of time, exchange current and double layer capacitance. It is shown as FUNCTION ETA(XT,IO,CAP) in the program LESSQ at the end of this section. The gamma functions which are necessary for the use of Equation 6 were read in as data in the main program and designated common with the FUNCTION ETA.

B. Curve Fitting

The object of curve fitting is to vary the parameters of interest, namely C_d and I_0 in a systematic way so as to generate a theoretical curve which agrees to a predetermined degree with the experimental curve in question.

The equation which must be minimized is:

$$Q(I_0, C_d) = \sum_{i=1}^{n} (y_i - Eta(x_i, C_d, I_0))^2$$
(8)

where y_1 is the experimental overpotential for the ith experimental time x_1 , and $\text{Eta}(x_1, C_d, I_0)$ is the theoretical overpotential at time x_1 for capacitance C_d and exchange current I_0 . If we approximate Eta by a multiple Taylor's series expansion of first order terms about the point $(I_0^{\circ}, C_d^{\circ})$, take the partials of Q with respect to C_d and I_0 and set them equal to zero, we obtain the equations which must be satisfied in order that the sum of the squares of the deviations be a minimum.

$$\sum_{i=1}^{n} [\mathbf{y}_{i} - \mathbf{ETA}_{i} - \Delta \mathbf{I}_{0} \frac{\partial \mathbf{Eta}_{i}}{\partial \mathbf{I}_{0}} - \Delta \mathbf{C}_{0} \frac{\partial \mathbf{Eta}_{i}}{\partial \mathbf{C}_{d}} \frac{\partial \mathbf{Eta}_{i}}{\partial \mathbf{I}_{0}} = 0 \qquad (9)$$

$$\sum_{i=1}^{n} [y_{i} - ETA_{i} - \Delta I_{0} \frac{\partial Eta_{i}}{\partial I_{0}} - \Delta C_{0} \frac{\partial Eta_{i}}{\partial C_{0}}] \frac{\partial Eta_{i}}{\partial C_{0}} = 0 \quad (10)$$

These Equations 9 and 10 are solved for ${}^{\Delta}I_0$ and ${}^{\Delta}C_d$, and the Gauss-Newton method which consists of the successive application of the formulas

 $I_{0(k+1)} = I_{0(k)} + \Delta I_{0(k)}, \quad C_{d(k+1)} = C_{d(k)} + \Delta C_{d(k)}(11)$ is applied.

To guarantee the convergence of the method, a modification of the Gauss Newton method by Hartley (29) is used. With this method

$$I_{0(k+1)} = I_{0(k)} + V_{\min} \Delta I_{0(k)}$$
(12)

$$C_{d(k+1)} = C_{d(k)} + V_{\min} \Delta C_{d(k)}$$
(13)

where V_{min} is defined by

 $V_{\min} = \frac{1}{2} + \frac{1}{4}(Q(0) - Q(1))/(Q(1)-2Q(\frac{1}{2}) + Q(0))$ (14) in which

$$Q(0) = \sum_{i=1}^{n} [y_i - ETA(x_i, I_{0(k)}, C_{d(k)})]^2$$
(15)

$$Q(\frac{1}{2}) = \sum_{i=1}^{n} \left[y_{i} - ETA(x_{i}, I_{0(k)} + \frac{\Delta I}{2}O(k), C_{d(k)} + \frac{\Delta C}{2}d(k) + \frac{\Delta C}{2}d(k) \right]^{2}$$
(16)

$$Q(1) = \sum_{i=1}^{n} [y_i - ETA(x_i, I_{0(k)} + \Delta I_{0(k)}, C_{d(k)} + \Delta C_{d(k)})]^2 \quad (17)$$

This method not only guarantees convergence, but it also reduces the number of iterations required for convergence. The partial derivatives of Eta were approximated by the relationships

$$\frac{\partial Eta}{\partial I_0} = \frac{Eta(I_0 + DI_0) - Eta(I_0 - DI_0)}{2DI_0}$$
(18)

$$\frac{\partial E t a}{\partial C_{d}} = \frac{E t a (C_{d} + DC_{d}) - E t a (C_{d} - DC_{d})}{2DC_{d}}$$
(19)

where DI₀ and DC_d were small fractions of the total value of the exchange current and capacitance respectively. It is possible to evaluate these derivatives analytically; however, the results are complicated and consume a significant amount of computer time to calculate.

These equations were incorporated in PROGRAM LESSQ written in FORTRAN IV for a Control Data 3600 computer. This program accepts experimental coulostatic data and computes the value of the exchange current and capacitance which produces the best fit with the experimental decay. Table A-I is a list of the data input for this program including dimensions which the data must have, and the program symbol.

Initial parameters were obtained from the slope and intercept of the first two experimental points. Iteration was terminated when the change in both of the parameters at the end of an iteration was smaller than some predetermined fraction of the variable before iteration. The output of the program includes the

TABLE A-I

PROGRAM LESSQ: DATA INPUT

Symbol	Definition	Units	
C(K)	Gamma functions	none	
со	Concentration of oxidized species	moles/cm ³	
CR	Concentration of reduced species	moles/cm ³	
DO	Diffusion coefficient of oxidized species	cm ² /sec	
DR	Diffusion coefficient of reduced species	cm ² /sec	
INC	Duration of applied pulse	sec	
т	Temperature	o _K	
CURR	Magnitude of applied current	amps	
AREA	Area of electrode	cm^2	
BN	Number of electrons trans- ferred in the electro- chemical process	none	
NX	Number of experimental points	none	
NN	Run number	none	
X(I)	i th experimental time	sec	
Y(I)	Experimental overpotential for i th experimental time	volts	
final curve fit value of the exchange current and capacitance, the concentrations, area of electrode, applied current, run number and a comparison of the overpotentials calculated with the final curve fit values of exchange current and capacitance to the experimental values.

```
3ETA=(LOGF(1000.+Y(2))-LUGF(100.+Y(1)))/(X(2)-X(1))
                               TYPE REAL IO.IDO.IU1.IU2.INC
Common Do.Dr.Co.Ch.Bn.T.Curr.R.F.Area.C(104).INC
                                                                                                 READ?, CO, CR, DO, UR, INC., T, CURK, AREA, RN, NX, NN
                                                                                                                                                                                                                                                                      ALPHA==BFTA+X(1)+LUGP(1000,+Y(1))
                                                                                                                                                                                                                                                                                                        CAP=(CURR/ETAU)/((10.*+4)*AKEA)
                                                                                                             FORMAT(5E8.2,3F10,0, 4, 3,0,213)
                                                                                                                                                                                                                                                                                                                        IOD=RETA+R+T+CAP/(UN+F)
                                                                READ 1, (C(K), K=1, 104)
               DIMENSION X(20), Y(20)
                                                                                                                                                                                                                                                                                                                                                          WRITE(61,1069)CAP.10
FUPMAT(2E20,8)
                                                                                                                                                                                   READ4.(Y(I).IE1.NX)
Format(lde8.2)
                                                                                                                                                  READ3, (X([), [=1, \X)
Format(10E9.2)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                CAP1=CAP+ <u>r</u>ü5+rap
                                                                                                                                                                                                                                                                                        ETAU=EXPF(ALPHA)
                                                                                 FORMAT(8F10,4)
                                                                                                                                  JF(ENF,60)40,5
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                102=10-,005+10
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                                                                                                                                                                                                                                                                                                                                         10=APSF(100)
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FURMAT(+-+,+RU'+,14,//,+CO=+,E15,6,8X,+CR=+,E15,6,8X,+CURKENT=+,
2F15,6,8X,+AREA=+,E15,8,//,+CAPACITANCE=+,E12,7,3X,+FAMADS+,5X,
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  3.EYCHANGF CJRHENT =+, E15.7, 5%, +AMPS+, //, +ETA JALC+, 16%, +ETA EXP+
                                                                                                                                                                                                                                                     DCAP=(SUMAI+SUMD-SUMAIBI*SUMC)/(SUMAIBI++2-SU4AI+SUMBI)
                                                                                                                                                                                                                                                                             0[0=(SUMA[B]+SUMD-SUM6[+SUMC)/(SUMA[+SUMB]-SUMA[9]++2)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           VMIN= P.50 + 0.25+(UZER0-00NE)/(00NE-2.+0HALF+7ZER0)
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                                               3[=(ETA(XT,10,CAP1)-ETA(XT,10,CAP2))/(.01+CAP)
                        A[=(ETA(XT,I')1.CAP)-ETA(XT,IO2,CAP))/(.01+10)
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                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       QZFH0=QZFR9+(Y(1)=ETA(XT,EX0,CD0))++2
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            00"E=Q0NF+(Y(1)-ETA(XT,EX2,CD2))++2
                                                                                                                                                  CBAR=AI+(ETA(XT, IU, CAP)-Y(I))
                                                                                                                                                                            DBAR=B1+(ETA(XT,1U,CAP)-Y(1))
                                                                                                                                                                                                                                                                                                     KRITE(41.1099) DCAP, UIO
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                                                                       SUMAI=SUMAI+AI++2
                                                                                               SUMB1=SUMB1+R1+*2
CAP2=CAP-,005+CAP
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                                                                                                                                                                                                                                 SUMC=SUMC+CBAR
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                                                                                                                                                                                                                                                                                                                                 FORMAT(2F20.8)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   CD2=CAP+DCAP
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FORMAT(E15.8, dX, E12. d, dX, E15.8)
                                                                                                                           JF(ABUCAP-,02+CAP)1U22,32,32
                                                                                                                                        IF (APIN-,01+10)1007,1007.32
                                                                                IF (NR. FQ. 6) GO TO 1007
                                                    ×RITE(61.1960)YC.YT.XT
                                                                                              ABRCAP=APSF(RCAP)
ABIC=ARSF(DIC)
                                        VC=ETA(XT, IJ, CAP)
- DO 53 1=1, NX
                                                                                                                                                        GO TA 160
            xT = x(1)
                          YT=Y([)
                                                                                                                                                                        E Z J
                                                                    1001
                                                                                                                                         1522
                                                      53
                                                                                                                                                                        4
```

```
FUNCTION ETA(X,10,CAP)

FUNCTION ETA(X,10,CAP)

TYPE RFAL T0,1NC

CUMMON D0,N4,C0,CM,BN,T,CURR,R,F,AREA,C(104),1NC

C1=0.0705230784

C2=0.0692705272

C3=0.0692705272

C4=0.0001520143

C5=0.0001520143

C5=0.0001520143

C5=0.0001520143

C5=0.0001520143

C5=0.0001520143

C4=0.0001520143

C4=0.0001520143

C5=0.0000430638

C4=0.0000430638

C4=0.000048047

C4=0.000040047

C4=0.000048047
```

```
1-1,+15,+7+(1,+17,*2+(~1,+19,+2+(1,+21,+2+(-1,+23,+2+(1,+25,+2+(-1,
                                                                                                                                                                                                                                                                                                              80=(w+(-1.+3.*w+(l.+).*w+(-1.+7.***(1.+9.***(-1.+11.***(1.+13.***(
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     3G=(Z+(-1.+3.+7+(1.+<sup>5</sup>.+Z*(-1.+7.*Z*(1.+9.*Z).-1.).+11.+2*(1.+13.*Z*(
                                                                                                                                                                                                                                 ERFXP=(1,+XP+(C1+XP+(C2+XP+(C3+XP+(C4+XP+(C5+XP+C6)))))++(-16,)
                                                                                                                                                                                                                                                                                                                                                                                                          EKFYP=(1.+YP+(C1+YP+(C2+YP+(C3+YP+(C4+YP+(C5+YP+C6)))))++(-16,)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            2FUNC=(1.+43)/(1./72454+YP)
                 IF (PTWD-ONF)640.58U, 28U
                                                                                                                                                                                                                                                                                                                                                                                       IF(YP-3.0) 594,594,595
                                                                                                                                                                                                              IF(XP-3.0) 592,592,593
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            XHFC=1./(AA-RU)*742HC
                                                                                                                                                                                                                                                  AFUNC=FXPF(XP2)+EHFXP
                                                                                                                                                                                                                                                                                                                                                                                                                           AFUNC=EXPF(YP2) +EKFYP
                                                                            A=(P+SRRTF4)/(2.*AN)
                                                                                               36=(P-SRRTE4)/(2.*AN)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    ABPKT=(1.-AFUNC)/AA
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      BBRKT=(1.-RFINC)/88
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         PRITHC=BHRKT-AGKKT
                                                       SRRTEM=SORTF(RTEY)
                                    RTEM=PTW0=4.+AN+3
QUO = ONF/PIWU
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    TEND=JNF-PTWO
                                                                                                                                                                                                                                                                                           x=1./(?.*XP2)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                    7=1./(2.*YP2)
                                                                                                                 SRT=SQPT(X)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 10 10 4001
                                                                                                                                                                                                                                                                         GO TO 596
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   50 10 591
                                                                                                                                                                                                                                                                                                                                                                                                                                                  30 10 591
                                                                                                                                     XP=AA+SHT
                                                                                                                                                                          x P 2 = X P + + 2
                                                                                                                                                                                              YP2=YP++2
                                                                                                                                                        YP=89+5RT
                                                                                                                                                                                                                                                                                                                                                                                        595
                                                                                                                                                                                                                                                                                                                                                                                                                                                                    595
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    ເ ິງ 🗸
                                                                                                                 589
                                                                                                                                                                                                                                                                                           593
                                                                                                                                                                                                                                                                                                                                                                                                          594
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            5012
                                    583
                                                                                                                                                                                                                                  2 9 2
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       194
```

```
5(H)=-(K-(S+H-3))+(K-(S+H-2))+(YP++2/XP++2)+6(H-1)/((2+H+2)+(2+H-1
                                                                                                                                                                                 IF (ARSF(YP)-1, n) 2005, 2004, 2004
IF (ABSF(YP)+ABSF(YP)-3,5)1011,3000,3000
                                                                                                                                                                                                                                                                                                                                                                                                                           xHFC=X¤FC+(-1)++(K+1)+(X/2,)+XRFX
                                                                                                                                                                                                                                                                                                                                                                                                                                           1 ( A 3 5 ( X 8 5 1) - 1 , 0 5 - 2 0 ) 1 0 4 , 1 0 2 , 1 0 2
                                                                                                                            IF (ARSF (YP)-3.0)1011.5000.3000
                                                                                                                                                1F(ARSF(XP)-1.0)2002.2003.2003
                                                                                                                                                                 IF (ABSF (YP)-2.7)1011, 3000.3000
                                                                                                                                                                                                                      IF (ASSF(XP)-2.7)1011.3000.3000
                                                                                                            IF (A9SF (XP)-,1)2000,2001,2001
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          0=+X++Z=Z++A++X+0=XUIt
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           9164=2**YP**3*6**YP**Z
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        7740=-77/(79++2+747+42)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              2##X5[c+2##X5]a=68w02
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      20,E=XF/(Xp++2+Y<sup>2</sup>++2)
                                                                                                                                                                                                                                                                                                                                                                                                                                                               IF(K-9R)103,104,104
                                                                                                                                                                                                                                                                                               C(4)=C.*X*XD**(X-1)
SHTEMP=SORTF(TEMP)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 CBM0J/N018-=54.1 A
                                   3=SRTEMP/(2.+AN)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                UAPONXULE = 144
                                                                                                                                                                                                                                                                                                                                                                                                          XKFX=SUMG/C(K)
                                                                                                                                                                                                                                                                                                                                                                                        SUNG=SUMG+G(M)
                                                                                                                                                                                                                                                                                                                                   FO 41, M=2, KK
                 A=P/(2.*AN)
                                                        SRT=SUFT(X)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     50 TO 401
                                                                                                                                                                                                                                                                                                                 SUMG=G(1)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    00 TO 101
                                                                          XP=SRT+A
                                                                                           YP=SRT+B
                                                                                                                                                                                                                                        X H F C = U . U
                                                                                                                                                                                                                                                                                XX== X+ X=
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   x || 7 + 4
                                                                                                                                                                                                                                                             ¥
11
11
                                                                                                                                                                                                                                                                                                                                                                         1))
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      104
3⊐0⇒
                                                                                                                               2002
                                                                                                                                                                                                                                                                                                                                                                                                                                                                  1 0 T
                                                        203
                                                                                                                                                2001
                                                                                                                                                                  2002
                                                                                                                                                                                                      2004
                                                                                                                                                                                                                        2003
                                                                                                                                                                                                                                                                               101
                                                                                                                                                                                                                                                                                                                                                                                         4
                                                                                                              2002
                                                                                                                                                                                     2003
                                                                                                                                                                                                                                           1011
```

```
ЯІ GYT2=7。+ХР++6+ҮР=32。+ХР++4+ҮР++3+21。+ХР++2+Ү¤++5-ҮР++7
СОМВЛ2=ВІ GXT2++2+Ы IGYT2++2
                                                                                                                                                                           3 [GXT2=XP++7-21,+XP++5+YP++2+35,+XP++3+YP++4=7,+XP+YP++6
                                                                                                                                                                                                                                                                                                                                                                                                                     3[GYT3=9<sub>**</sub>XP*+8*YP=84<sub>*</sub>*XP*+6+YP*+3+126<sub>*</sub>*XP*+4+Y<sup>2</sup>++5
                                                                                                                                                                                                                                                                                                                                                      RIGXT3=XP++9-36.+XP++7+YP++2+126.+XP++5+YP++4
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      D=+(77w0+YI446+YIMA41+YIMA62+YIMA63)/1.772454
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            FIA= ETATO-(ETAIJ+AH<sup>f</sup>C+[U+Ah+F)/(R+T+CAP)
8[GXT=XP++5+10 + ××++3+YP++2+5, +×P++4
3[GYT=5, +×P++4+YP+10; +×P++2+YP++5
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    C= (ZONF+XRI,+XKI, 1+XKL 2+XHLT3)/1.772454
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 V [ MAG3= (-105, + RISYIS) / (10, + COMBO3)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             XRLT3=(105,*RIGXT3)/(16,*COP803)
                                                                                                                                                                                                                                                                                 XRLT2=(-15,+815XT2)/(8,+C0M602)
                                                                                                                                                                                                                                                                                                                   Y I MAG2= (15, + RIGYT2) / (8, + COMBO2)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         xRFC=(P=8+C-A+D)/(0+A+2+8++3)
                                                                                                                                         VIMAGT=(-3.+RIGYT)/(4.+CUMRCT)
                                                                                                                                                                                                                                                                                                                                                                                          1=84 * × P * * 3 * Y P * * 6 + 9 * * X P * Y P * • 8
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        ETATO=(CURR+INC)/(CAP+AREA)
                                                                                                        xRLT=(3.+BIGXT)/(4.+COMBUT)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            CUMB73=B1GXT3++2+B1uYT3++2
                                                                    COMB0T=BIGXT++2+314Y [++2
                                                                                                                                                                                                                                                                                                                                                                                                                                                            1-36.*XP**2*YP*+7+YP*+9
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      NULLE
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      2
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               4000
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 4061
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APPENDIX B

COMPUTER PROGRAM FOR NUMERICAL CALCULATIONS ON THE GALVANOSTATIC TECHNIQUE

The equations used to calculate theoretical

<u>vs</u>. t curves for the galvanostatic technique are very similar to those of the coulostatic technique. Equation IV-2 could be expressed in terms of the same series in only a slightly altered form. FUNCTION ETA(X,IO,CAP) written in FORTRAN IV computes the value of the overpotential for a given value of X (time), exchange current (IO), and CAP (double layer capacitance).

This function was combined with a slight modification of PROGRAM LESSQ to curve fit experimental data. It was necessary to read in initial estimates of the exchange current and capacitance since there is no easy way to estimate the exchange current from short time measurements.

137

```
1-1.+15.***f1.+17.*W*(-1.+19.*W*(1.+21.*W*(-1.+23.***f1.+25.***f".
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 AQH("***+1.+3.+W+(1.+5.****(*1.+7.*W+(1.+9.*W***)).+11.+11.+14.(1.+13.****
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           FXfXf={1.+xp*(C1+Xp*(C2+XP*(C3+XP*(C4+XP*(C5+XP+C6)))))+*(-16+)
FU"CTIIN ETA(X,In,CAP)
CO4PLEx 71,22,SUMEX1,SUMEX2,EXER1,FXER2,WZ1,WZ2,PR,PRN,Z3,Z4
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             CO 4MON D1, DR, C0, CR, 3N, T, SURR, R, F, C(104)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  AF IN-=(1.+40)/(1.77245+X-)
                                                                                                                                                                                                                                                                  JEV12=(1./TEV1)+(1./TEV2)
                                                                                                                                                                                                                                                                                                                                  0=([BN+F/(B+T])+(]0/CAP))
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            IF (YE- 4. n) 594, 504, 505
                                                                                                                                                                                                                                                                                         (3+N8+"2)/(2]N32+0])=d
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        1F1XP-1.1) 592,592,593
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    AF INC==XPF(XP2)+ERFXP
                                                                                                                                                                                                                                                                                                                                                        IF (PTW)-7)500,580.580
                                                                                                                                                                                                                      PEV1=C3+(SART(PD))
                                                                                                                                                                                                                                          nEv2=Ca+(SORT(DR))
                                                                                                                                                                                                                                                                                                                                                                             (U-UMLd)LeCs=nHsLA
                                                                                                                                                                       C5=C.01C2745672
C6=0.0101430438
                                                                                     C1=0.0705230784
                                                                                                                               c3=0.01927ñ5272
                                                                                                                                                 C4=0.0101520147
                                                                                                           C2=0.0422820123
                                         REAL 13, PRNTHC
                                                                                                                                                                                                                                                                                                                                                                                                                      GAUMA=2-YTER4
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 W= 4 . / ( 2 . • X ¤ 2 )
                                                                                                                                                                                                                                                                                                                                                                                                     RETA=P+YTEDM
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           YP=GAM4A+SPT
                                                                                                                                                                                                                                                                                                                                                                                                                                               SRTESQATIXI
                                                                                                                                                                                                                                                                                                                                                                                                                                                                    XP=BETA+SRT
                                                                                                                                                                                                                                                                                                             5++c=UM1d
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           GU TO 595
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               YPJ=YP++2
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    YP2=VP++2
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          595
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 593
                                                                                                                                                                                                                                                                                                                                                                                                                                               588
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               597
                                                                                                                                                                                                                                                                                                                                                                              530
```

```
RU=(7+(-1,+3,+7+(1,+5,*2+(-1,+7,*2+(1,+9,*7+(-1,+11,*2+(1,+13,*2+(
1-1,+15,*7+(1,+17,+7+(-1,+19,*2+(1,+21,*2+(-1,+23,*7+(1,+25,*2+(-1,
2+27,*2+(1,+29,*2+(-1,+31,*2))))))))))))))))))
FKrYp=(1.+Yp+(r]+Yp+(C2+YP+(C3+YP+(C4+YP+(r5+YP+r6)))))))))++(=16.)
                                                                                                                                                                                      ABJKT=(GAMMA/(RETA++2))+(AFUNC+(2.+BETA+SRT/1.772454)-1.)
RBJKT=(BFTA/(GAMMA+2))+(BFUNC+(2.+GAMMA+SRT/1.772454)-1.)
PKWTUC=(ABJKT-RBPKT)/(GAMMA-BETA)
                                                                                                                                                                                                                                                                                                                                                                                                                                                             IF(CABs(71)-3.5)1011.3000.3000
Su4EX1=(0.1.0.1)
                                                                                                                                                RF JNC=(1.+RQ)/(1.772454+YP)
                       RF JNC= EXPF (YD2) + FRFYD
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  EX#R2=((-22)++K)/C(K)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            EX=R1=((-21)++K)/C(K)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       SUVEY2=SJMFX2+FXFR7
SUVEY2=SJMFX2+1.n
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              SUVEX1=SUMFX1+FXFR1
SUVEX1=SJMFX1+1.n
                                                                                                                                                                                                                                                                                                                                                              21=CWP_X(XP,YP)
72=CWP_X(XP,YP)
73=CWP_X(P,YTERM)
74=CWP_X(P,YTERM)
                                                                                                                                                                                                                                                                              YTERVESORT(O-PTWO)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   SUVEX2=(1. ñ. ñ. ñ.
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   SUMEX1=(P. ñ. n. ñ)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               (C++12+C)/(S+21++2)
                                                                  7=1./(2.+402)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       DU 76 4=1,98
                                                                                                                                                                                                                                                                                                                                            YP=SPT+YTERM
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 P. 7 4=1, 75
                                                                                                                                                                                                                                                                                                   SAT= COPT(X)
                                                                                                                                                                                                                                                          50 Tr 4011
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               GO TC 3999
                                                                                                                                                                        GU Tr 591
                                           GO TO 391
                                                                                                                                                                                                                                                                                                                       XP=S¤T+P
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          D.=1.0
                                                                 595
  594
                                                                                                                                                                                                                                                                                5
0
9
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                75
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   300.
                                                                                                                                                                                             591
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    1011
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       77
```

```
3999 PR=(74/(73+*2))+(SUMFX1+(2+*23+SRT)/(1,772454)-1.)
1 -(23/(24+*2))+(sUMEX2+(2+*24+SRT)/(1,772454)-1.)
                                                                                                                                                                                  SU"EX2=SJMEX2+(1./(Z2+1.772454))*EYER2
SU"EX2=SIMEX2+1./(72+1.772454)
                            SU4EX1=SJMFX1+(1./(Z1+1.772454))+EYER1
SU4EX1=SJMFX1+1./(71+1.772454)
SU4EX2=(0.5.0.0)
                                                                                                                                                                                                                                                                                                     ETA=(CJR3/CAP)+PANTHC
                                                                                                                                                  NJ=DJ+{2+K=1)
Exsr2=J+(=#72)++K
                  EX5R1=JJ+(=W21)++K
                                                                                           wZ2=1./(?+72++?)
DJ=1.0
                                                                                                                                                                                                                                                                  PAWEPR/(74-23)
PJ=DJ+(2+K-1)
                                                                                                                                 PU 79 4=1,15
                                                                                                                                                                                                                                                                                    PRATICEPUN
                                                                                                                                                                                                                                                                                                                           Na∩⊾∃a
                                                                                                                                                                                                                                                                                                                                             с
2.
Ш
                                      78
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