Quarterly Technical Report

on

DIRECT ENERGY CONVERSION SYSTEMS

Part II

ELECTROCATALYTIC ACTIVITY OF HYDRAZINE
IN FUEL CELL APPLICATIONS

Prepared for
Advanced Research Projects Agency

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Mechanical Engineering Department

**STANFORD UNIVERSITY ▪ STANFORD, CALIFORNIA**

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# ABSTRACT

The electrode reactions of hydrazine in acid and basic solutions on smooth and platinised platinum have been examined. From analysis of the rest potentials and concentration relationships a rapid one electron exchange with a stable surface species has been postulated. The mechanism of oxidation occurs via a sequential system whereby hydrazinium radicals are the products of the initial oxidation.

The electrode reactions of carbon monoxide in acid solutions on smooth platinum electrodes have also been examined. The carbon monoxide is strongly bound to the metal surface and probably exists as a compound. Suppression of the reversible hydrogen reaction was observed in the presence of CO. Removal of the carbon monoxide film was performed as soon as oxide formation occurred indicating that the carbon monoxide is essentially electro-inactive and that the reaction is purely chemical with the metal oxide to form carbon dioxide. Electrochemical regeneration of the metal oxide forms the regenerative cycle.

$$MO + CO \rightarrow M + CO_2$$
$$M + H_2O \rightarrow MO + 2H^+ + 2e^-.$$

The oxidation of methanol in acid does not proceed via carbon monoxide as an intermediate.

## Electrode Reactions of Hydrazine

As a potential fuel for fuel cell studies, hydrazine is convenient as it is soluble in the electrolyte and stable, thus eliminating the problems of triple phase studies using porous electrodes. Preliminary work on the electro-oxidation has indicated that the reaction is rapid over the total four electron steps.

i.e.,
$$N_2H_5^+ \longrightarrow N_2 + 5H^+ + 4e^- \tag{1}$$
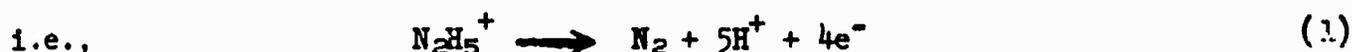
Although several workers have examined this system in both acid and alkaline media, there is considerable disagreement between authors. Pavela,[1] working in alkaline media on platinum and gold, concluded that the juxtaposition of the reversible hydrogen potential was the most significant factor and that the hydrogen atoms were stripped from the hydrazine molecule and subsequently oxidized, giving an over-all mechanism of a low pressure hydrogen electrode. Recently, Baker and Eisenberg[2] came to the same conclusion as Pavela, indicating that the hydrogen discharge was rate controlling.

In conflict with this view were the works of Meites and Karp[3] and of Bard[4] where the effect of the surface state of platinum electrode was investigated and consideration was made for an intermediate redox system using the platinum oxide (or hydroxide) to facilitate the reaction.

e.g.,
$$\left. \begin{array}{c} 2(Pt + H_2O \longrightarrow PtO + 2H^+ + 2e^-) \\ 2PtO + N_2H_5^+ \longrightarrow 2Pt + N_2 + 2H_2O + H^+ \end{array} \right\} \tag{2}$$
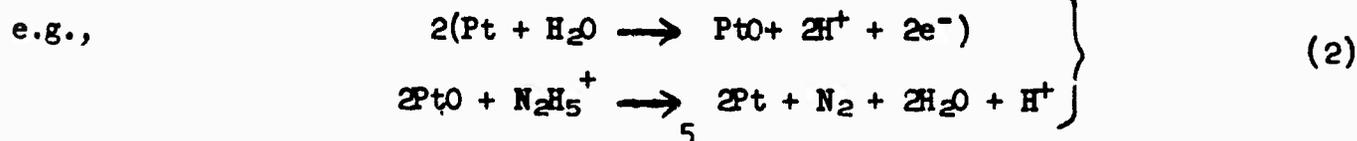
Finally, Susbielles and Bloch[5] considered the presence of two concurrent reactions, one being the oxidation of hydrazine while the other was the reaction of the electrolyte.

e.g.,
$$\left. \begin{array}{c} N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^- \\ 2H_2O + 2e^- \longrightarrow 2OH^- + H_2 \end{array} \right\} \tag{3}$$
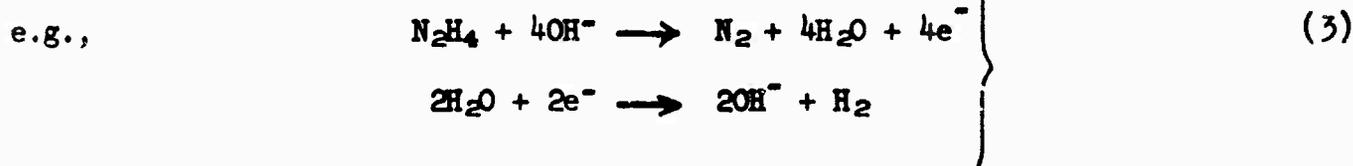
## EXPERIMENTAL

Examination of the reactions of hydrazine were carried out in both acid and alkaline media with platinised platinum and smooth platinum electrodes. To examine the potential - concentration of hydrazine charac-

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teristics - a thin film cell similar to that of Anson and Christiansen was built. Details of this technique are given in Appendix I. With this technique, there can be no effective bulk of solution as the electrolyte is spread only in a thin film on the surface of the electrode.

The surface characteristics of the electrode in the presence of hydrazine were examined using the classical Faradaic impedance technique. Details of the apparatus and essential theory are given in Appendix II.

To examine the kinetic rate of the reaction, the coulostatic pulse technique was utilized. Here a rapid pulse is applied to the electrode surface and the consequent potential rise and decay are recorded on an oscilloscope. Details of the experimental arrangement and theory are given in Appendix III.

## RESULTS AND DISCUSSION

Initially, an examination of the rest potential as a function of pH was carried out. A constant hydrazine concentration of $0.02\underline{N}$ and ionic strength of 1.0 using sodium perchlorate was used; the pH values were obtained by dilution of perchloric acid or sodium hydroxide. The hydrazine was diluted from a concentrated bulk solution and titrated with iodate by the Andrews' method. The results of the rest potential on platinised platinum are shown in Figure 1, line A, whilst the values of the rest potential on smooth platinum are shown on line B. On smooth platinum in alkaline solutions, the reproducibility was very poor in the absence of

stirring. With agitation, the rest potentials shifted to more positive values; usually of the order of 20 mV more positive. This result in itself indicates that the potential is not controlled by any one electrode reaction but is some compromise of at least two and possibly several concurrent reactions which may be significantly affected by mass transport and particularly the surface characteristics of the electrode governing adsorption.

The over-all change in potential of the rest potentials on platinised platinum with pH is 45 mV per pH unit. Also indicated on Figure 1 is line C. This is the change of the reversible hydrogen potential with pH. Convergence of the rest potentials of the hydrazine reaction on platinised platinum, with the reversible hydrogen potential at higher pH's is quite clearly seen. The values for the rest potential of hydrazine on smooth platinum lie so far to the positive side of the hydrazine rest potentials on platinised platinum that the two controlling reactions cannot be anywhere near the same. As will be shown later, the surface concentration of hydrazine on platinised platinum and smooth platinum in both acid and alkaline solutions is essentially zero at potentials of +100 mV with respect to the rest potential of the system in the same solution. With respect to the latter point, it is of considerable interest to note differences between the potentials of hydrazine oxidations on smooth platinum and those on platinised platinum at the same pH values and the same hydrazine concentrations. There was no difference to be shown between platinised platinum prepared by different methods or degree of platinisation. Indeed, the difference in rest potentials between smooth platinum

and platinised platinum was about +200 mV. It is clear, therefore, that significantly different controlling reactions exist for these two surface states. Using a high impedance measuring system to record the electrode potential as a function of time, the potential of a smooth platinum electrode was found not to change on sudden immersion in the hydrazine solution. The platinised platinum electrode however, showed an initial potential on sudden immersion that was the same as that obtained with smooth platinum. The potential then decayed progressively to more negative values (towards the reversible hydrogen potential) until after five minutes a steady value was obtained, the total deviation being the 200 mV difference previously mentioned. The rate of decay did not appear to be affected by mass transport, as evidenced by the insensitivity of bubbling of nitrogen through the solutions. It must be supposed that the catalytic value of the platinised platinum surface produced some species from the hydrazine reaction to modify the surface, or that the surface became modified by the hydrazine reaction and presented essentially a non "platinum" electrode - one having electrocatalytic properties very different from smooth platinum.

In order to examine the potential vs. hydrazine concentration characteristics in the absence of mass transport, a series of thin film chronopotentiograms were obtained at high and low pH's and all having an initial hydrazine concentration of $0.02\underline{N}$ and unity ionic strength. In all cases, total quantitative consumption of the hydrazine was obtained. The potential time curves are shown in Figure 2. At low pH's (pH = 0, 1, 2) a series of smooth curves were obtained, with very little change in potential at low current densities. These curves were fitted to a function of E vs. constant $\log \dfrac{T}{T-t}$ where $T$ is the transition time required for complete
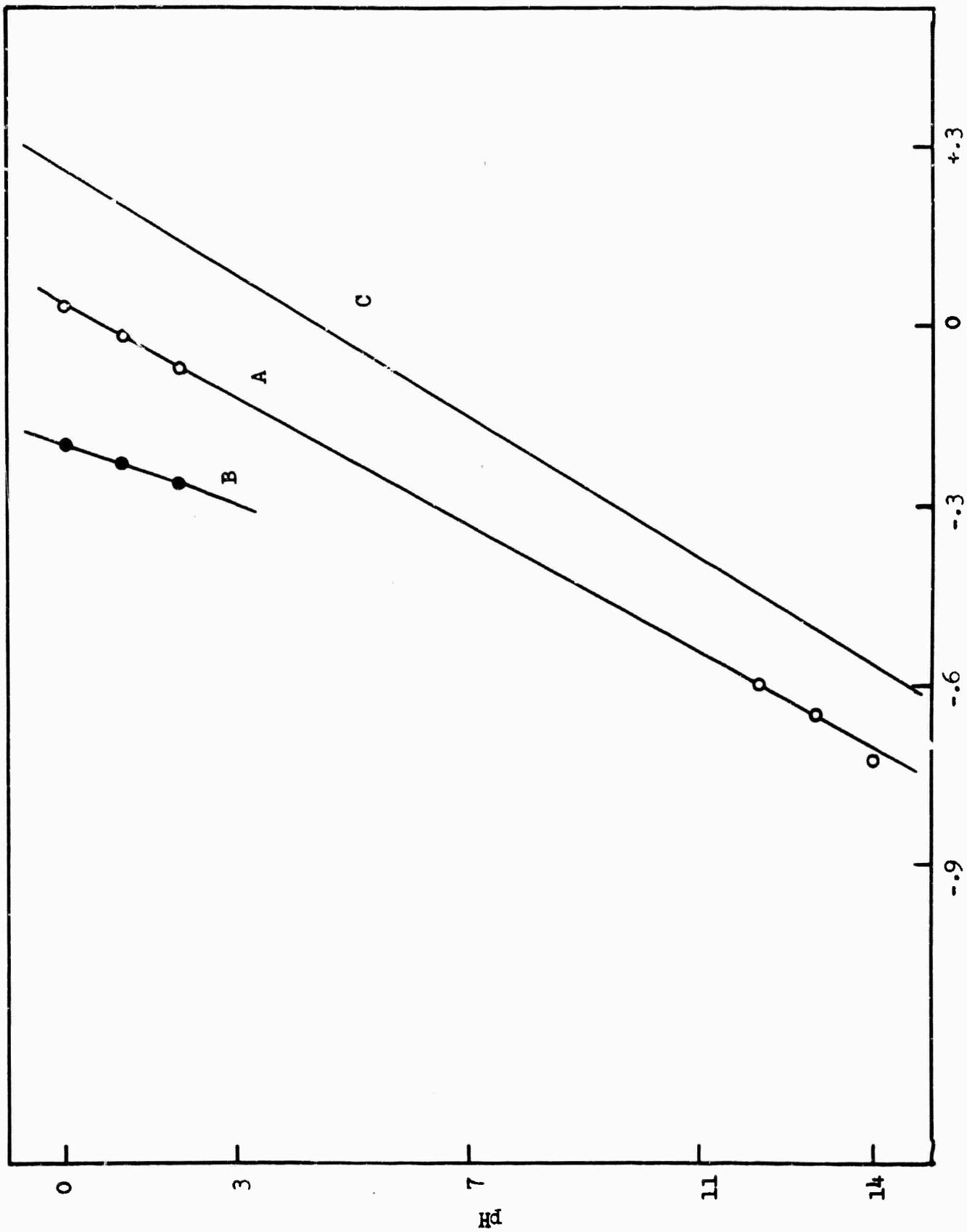
Rest Potential vs. S.C.E.

Rest Potentials of 0.02M N₂H₄ Solutions on Platinum
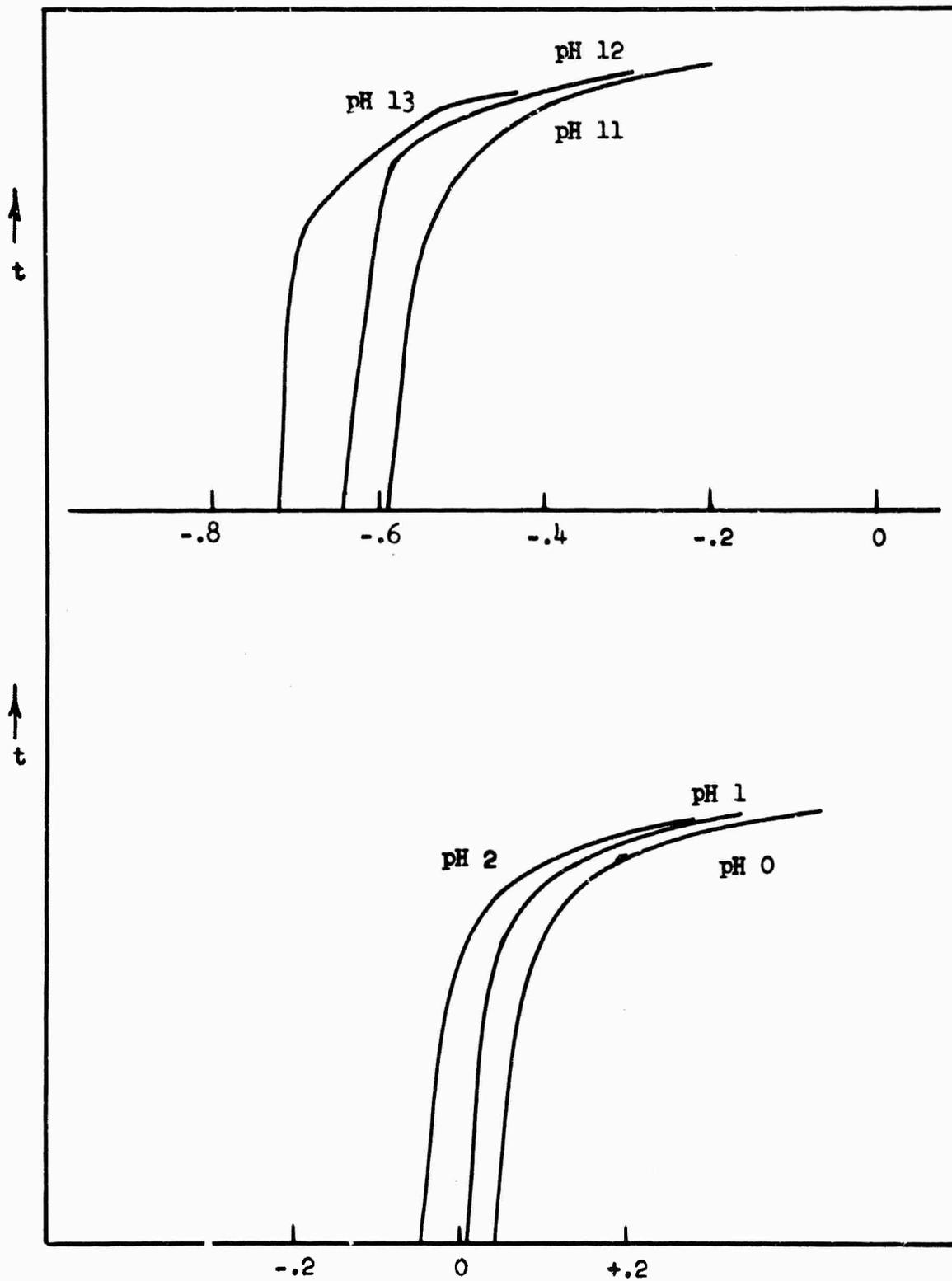
Figure 1

Figure 2            Potential vs. S.C.E.

Thin Film Chronopotentiograms of 0.02N $N_2H_4$ on
Platinised Platinum

consumption of the hydrazine within the thin film cell and t is any inter-
mediate time up to $\tau$ (Appendix I). One such t - E curve is shown in
Figure 3. The transition time $\tau$ is well evidenced and linearity to
$\log \frac{\tau}{\tau - t}$ within experimental accuracy is good.

On the basis of these results alone, we might say that in acid
solutions a reaction for the oxidation of hydrazine occurs, whereby either
the surface of the electrode acts as one species of a reversible couple
with the hydrazine in the solution, or that at very small current densities
there is primary formation of an adsorbed species which completely covers
the electrode surface and becomes potential controlling by means of the
change in hydrazine concentration within the solution. There is some
evidence for this, in that on initial passage of the current density, a
rapid change of about +20 mV is obtained which is too great to explain
by IR drop or by simple galvanostatic perturbations considering the low
overpotentials subsequently obtained for progressive consumption of the
hydrazine. Examination of $\Delta E / \Delta \log \frac{\tau}{\tau - t}$ showed two values. At low
orders of t a value of 60 mV was obtained, whilst at higher values of
t a value of about 70 mV was obtained. If is probably that these values
at higher t are high due to microscopic bubble formation of nitrogen
within the thin film cell and hence displacing small quantities of
electrolyte from the cell. In this manner, the total volume of solution
in the cell at the termination of the experiment was very slightly less
than at the start and that calculated. It is believed that this explains
the change in slope of the E vs. $\log \frac{\tau}{\tau - t}$ plot. From the value of
60 mV for the $\Delta E / \Delta \log \frac{\tau}{\tau - t}$ a one electron reversible reaction that
is surface controlled is postulated and will be discussed at a later
stage.
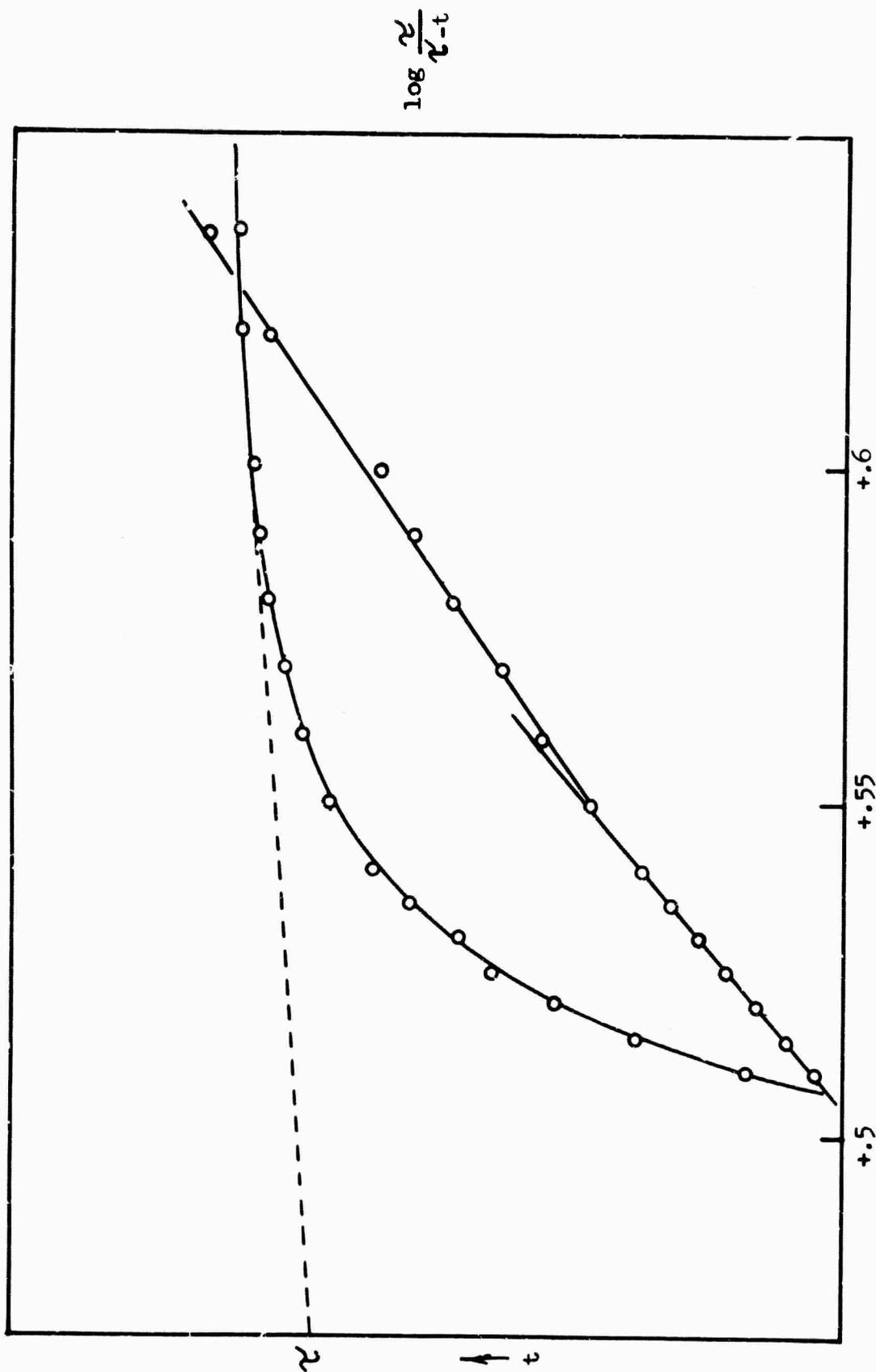
Figure 3

Potential vs. N.H.E.

Thin Film Chronopotentiogram of 0.02M $N_2H_4$ in 1N $HClO_4$ on
Smooth Platinum. Function of Time and Log Plot

At high pH's (pH = 14, 13, 12, Figure 2) t - E curves are no longer smooth transitions but show "knees" and flat regions although, as in the acid region curves, good stoichiometric consumption of the hydrazine within the cell was obtained. The only explanation for the appearance of these "knees" is that as the potential changes with removal of the hydrazine in solution, the rate controlling mechanism changes to a mechanism having different overvoltage $(\eta)$ vs $[N_2H_4]$ characteristics. This factor shows that the oxidation of hydrazine is controlled by no one simple step but rather by either a mixed potential system as advocated by Susbielles and Bloch or by sequential oxidation steps derived from the product of the initial oxidation of the hydrazine, at the electrode surface. Owing to the positive potentials obtained with respect to the reversible hydrogen reaction in the same solution, we may say that the rate most certainly is not controlled by hydrogen oxidation as supposed by Pavela and by Baker and Eisenberg.

In order to examine more closely the surface effects of the platinum in the presence of the hydrazine raction, a series of experiments were conducted to measure the complex Faradaic impedance of the electrode as a function of frequency of the A.C. signal and of potential. The results of a typical determination on smooth platinum in $1\underline{N}$ $HClO_4$ are shown in Figure 4. The impedance was measured as a series capacitance and resistance, no extraction of the double layer capacity of platinum in $1\underline{N}$ $HClO_4$ at the same potentials in the absence of hydrazine being performed. Data on the complex impedance of platinum in perchloric acid solutions is presented at a later stage in this report. The acid region was chosen for impedance examination as this gave the greatest divergence from the impedance resulting from the reversible hydrogen reaction.
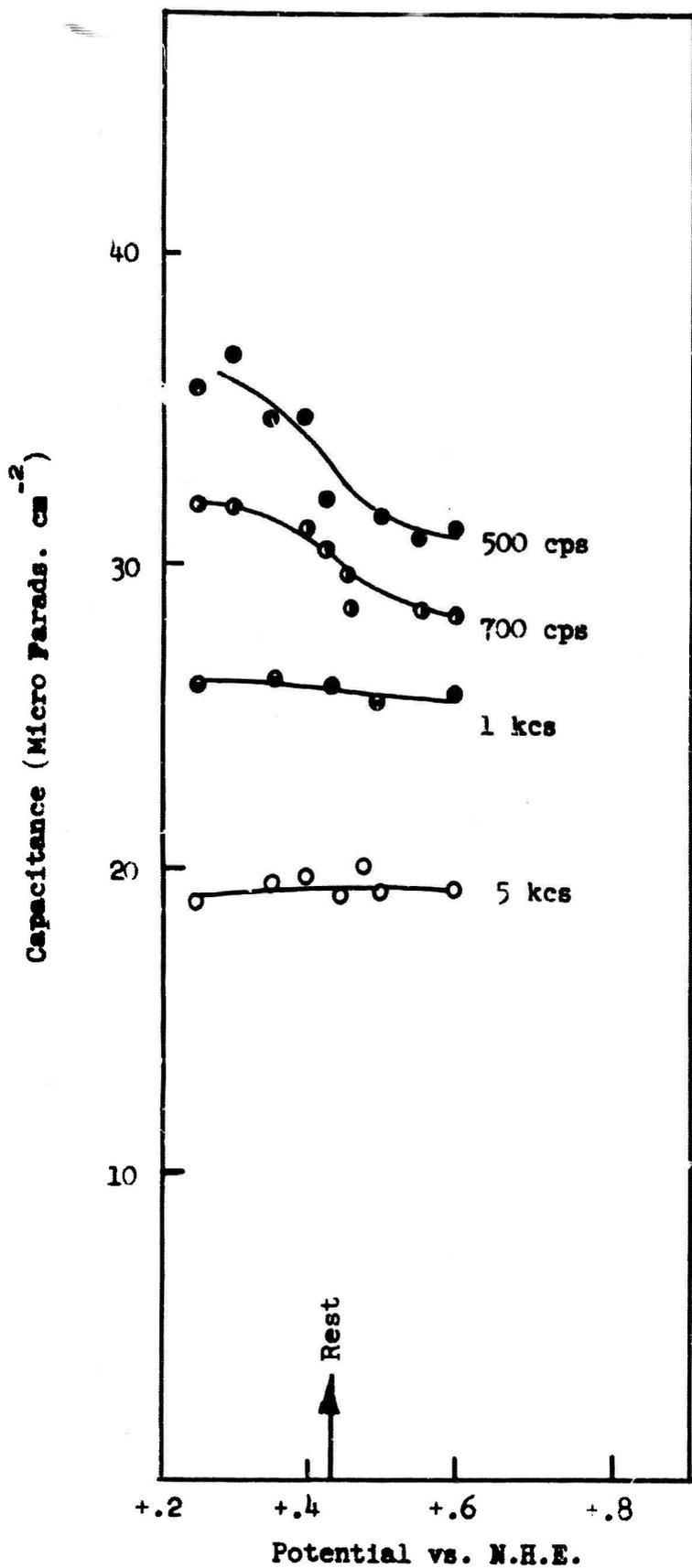
Figure 4A
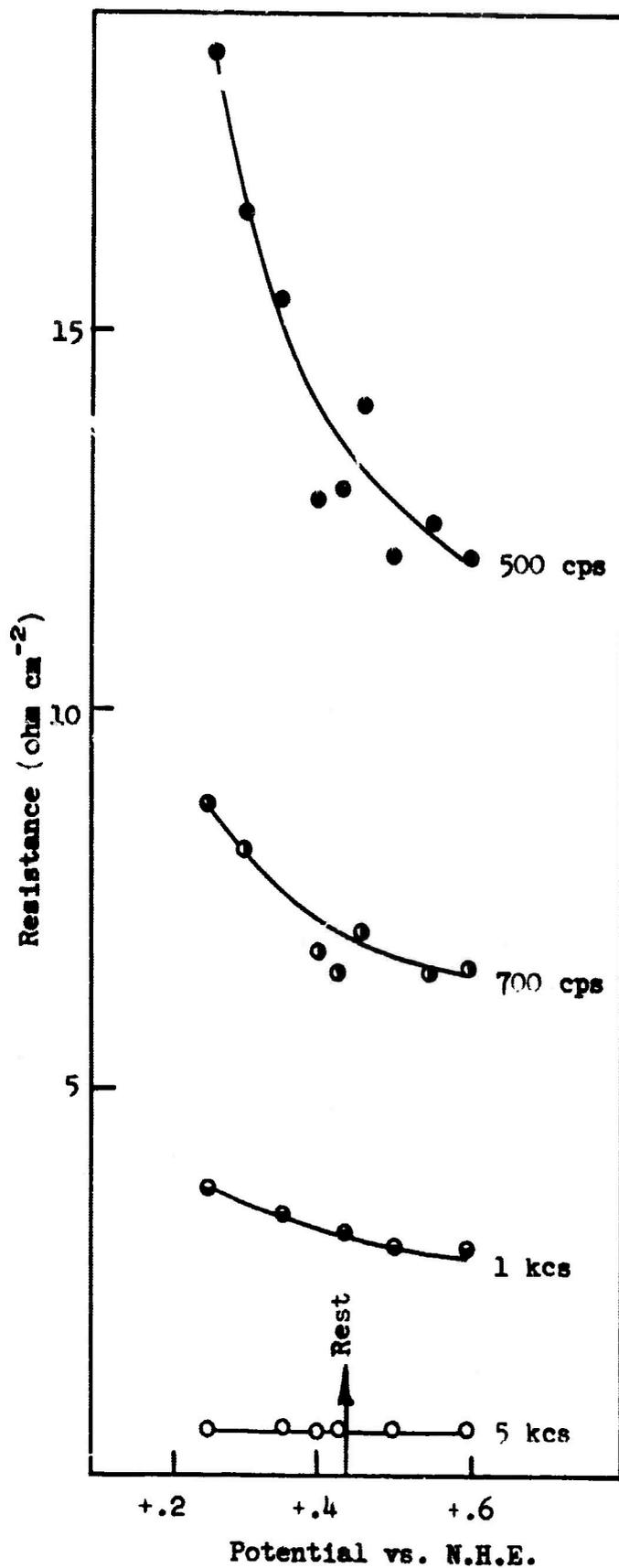
Figure 4B

Impedance of Smooth Platinum in 1N HClO₄ Containing 0.2N N₂H₄.

From the experimental results presented, it may be seen that both the capacitative fraction of the impedance and the resistive fraction decrease significantly on passing to more anodic potentials; or rather as the ..ydrazine oxidation proceeds. The data is consistent with formation of an adsobed film at the electrode surface concurrent with the hydrazine oxidation. At the most positive potentials shown of +.6V vs. Normal Hydrogen Electrode (NHE) the surface concentration of hydrazine is essentially zero, a conclusion obtained from the thin film data. It would seem however, that there may be some residual adsorbed species remaining on the surface or possibly that the hydrazine is diffusing to the electrode at the sufficient rate to modify the electrode surface and prevent initiation of oxide formation.

As the Faradaic impedance system did not indicate any peaking at the rest potential of the electrode, associated with the diffusional impedance of hydrazine to the electrode, the kinetic rate was measured using coulostatic pulses (Appendix III). The pulses were applied to both smooth platinum and platinised platinu. in perchloric acid solution. On smooth platinum, no difference could be observed between the relaxation values obtained in the presence of hydrazine and in the absence of hydrazine at the same potential; shown in Figure 5. On this basis it was supposed that the rate of the electrode reaction was controlled by the rate of some surface platinum oxide or hydroxide as discussed by Meites and Karp and by Bard. On platinised platinum, however, the rate of decay of the pulse in the presence of hydrazine was significantly greater than the decay at the same potential in the absence of hydrazine.

a.

b.



Figure 5.  a.  0.02$\underline{N}$ $N_2H_4$ in $1\underline{N}$ $HClO_4$

x axis 10 µs; .1 ms; 1 ms; 10 ms per division

b.  $1\underline{N}$ $HClO_4$.  Same potential as a.

x axis 10 µs; .1 ms; 1 ms; 10 ms per division.

Data on the kinetic rate constant $k$ is presented in the following Table I.

## TABLE I

| E vs. S.C.E. (volts) | $[N_2H_4]$ (moles $cm^{-3}$) | $[H^+]$ (moles $cm^{-3}$) | $-\phi$ | $k$ (cm $sec^{-1}$) |
|---|---|---|---|---|
| +.027 | $0.02 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | $2.24 \times 10^{-7}$ | $3.14 \times 10^{-3}$ |
| -.0202 | $0.2 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | $1.35 \times 10^{-6}$ | $3.87 \times 10^{-3}$ |
| +.003 | $0.02 \times 10^{-3}$ | $0.1 \times 10^{-3}$ | $3.18 \times 10^{-7}$ | $9.30 \times 10^{-3}$ |
| -.067 | $0.2 \times 10^{-3}$ | $0.1 \times 10^{-3}$ | $5.44 \times 10^{-7}$ | $1.59 \times 10^{-2}$ |
| -.015 | $0.02 \times 10^{-3}$ | $0.01 \times 10^{-3}$ | $3.00 \times 10^{-7}$ | $1.89 \times 10^{-2}$ |
| -.117 | $0.2 \times 10^{-3}$ | $0.01 \times 10^{-3}$ | $3.92 \times 10^{-6}$ | $5.33 \times 10^{-2}$ |

In Table I are the potentials of measurement of the rate constant, the pertinent concentration of hydrazine, the perchloric acid concentration and the term $\phi$ derived from the relaxation of the coulostatic pulse exluding the concentration terms of reactant and product. This term $\phi$ is related to the rate constant in the following manner:

$$\frac{\Delta \log \eta}{\Delta E} = \frac{-k}{C_{dl}^*} \cdot \frac{n^2 F^2}{2.303 RT} \cdot [c_1]^{\alpha} [c_2]^{1-\alpha} \qquad (4)$$

where $\Delta \log \eta$ is the initial change in the overvoltage as a function of the change in Time $\Delta E$, k is the specific rate constant and $C_{dl}^*$ is the experimental double layer capacity value obtained under the experimental conditions. The concentration of the oxidised species is $C_1$ and the concentration of the reduced species is $C_2$ where $\alpha$ is the transfer coefficient, assumed to be 0.5 and $\dfrac{n^2 F^2}{2.303 RT}$ are the usual electrochemical constants.

$$\text{Then } k = \frac{-\Delta \log \eta}{\Delta E} \cdot c_{dl}^* \cdot \frac{2.303\, RT}{n^2 F^2} \cdot \frac{1}{[c_1]^\alpha [c_2]^{1-\alpha}} \tag{5}$$

$$= -\phi \cdot \frac{1}{[c_1]^\alpha [c_2]^{1-\alpha}} \tag{6}$$

The value for k presented, assumes that this is the rate of
the electron transfer step and that the reaction is first order in
hydrazine and a single electron step. This follows from the data
obtained using the thin film cell. If this step is fast, then rever-
sibility should be obtained and the reaction to be of the type

$$N_2H_5^+ \rightleftharpoons \text{products} + H^+ + e^- \tag{7}$$

Taking into consideration the hydrogen ion concentration,
no simple relationship is obtained for the relation of k to the potential
of measurement, provided a concentration term of less than unity is used
for the reaction products as written above. If the surface concentration
is considered unity for the situation

$$\left. \begin{array}{l} N_2H_5^+ \rightleftharpoons N_2H_4^+ + H^+ + e^- \\ c_1 \rightleftharpoons c_2 \qquad c_3 \end{array} \right\} \tag{8}$$

$$\text{and } k = -\phi \cdot \frac{1}{[c_1]^\alpha \cdot [c_2]^{1-\alpha} [c_3]^{1-\alpha}} \tag{9}$$

and assuming $\alpha = 0.5$ and $c_2 = 1.0$ then

$$k = -\phi \cdot \frac{1}{3\sqrt{[N_2H_5^+] \cdot [H^+]}} \tag{10}$$

These values of k are presented in Table I.

For this assumption to be correct, the adsorbed film of the
electrode surface must be so strongly bonded that there cannot be any
equilibrium with the bulk solution, meaning that desorption is very
slow.

Although data for the rate constant have been presented, it is not certain that complete separation of the conflicting mechanism of the reversible hydrogen reaction has been attained. Indeed in the solution of 0.2 M hydrazine and 0.01 M perchloric acid the reaction potentials are very close and it may be presumed that for these conditions, considerable influence on the measured rate constant for the hydra: oxidation reaction is obtained from the interfering hydrogen reaction. This condition does not have such a great effect on the other experimental values obtained.

Finally, a series of experiments were performed to observe the effect of polarising the electrode in a cathodic direction, that is, towards the reversible hydrogen potential. At low constant current densities the potential changed rapidly, as was expected, until hydrogen evolution occurred. On interuption of the current and allowing the electrode to relax, a rapid decay of the electrode potential was observed that proceeded to "overshoot" the previous rest potential before coming back to a final value in agreement with that potential originally obtained. This is most clearly seen in Figure 6. The length of time that the potential "overshot" the final rest potential was a function of the potential to which it had been polarised in the cathodic direction prior to relaxation. For small polarisations there was little or no effect, whilst as cathodic polarisation was increased, the corresponding magnitudes of the "overshoot" also increased. No different relaxation time effects between situations where the electrode had been held at a given potential for a period and those where the electrode had been rapidly set to the same potential could be observed. From these results,
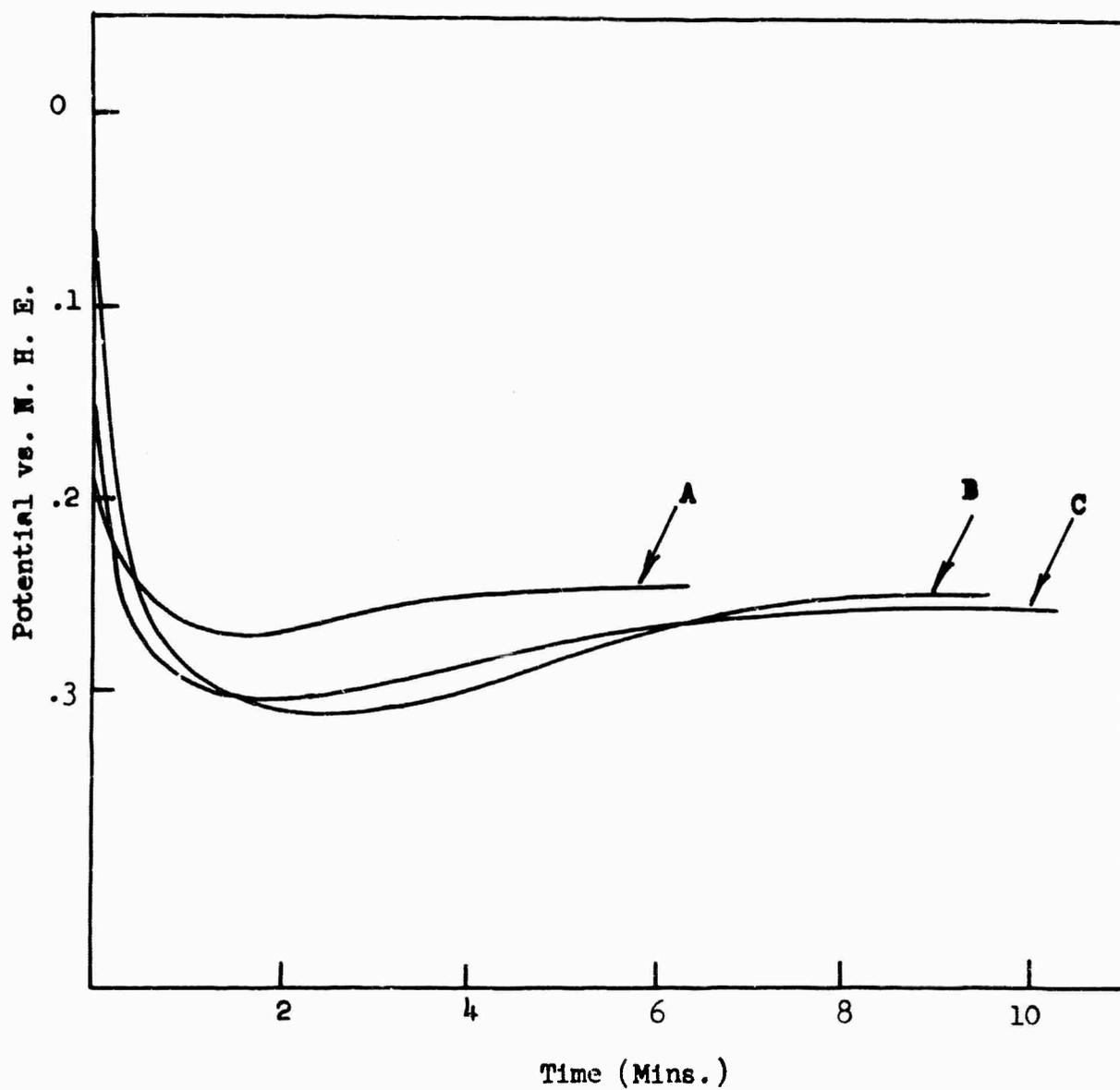
Figure 6. Relaxation after Cathodic Polarization of Platinised
Platinum Electrode in $1\underline{N}$ HClO$_4$ Solutions Containing $0.2\underline{N}$ N$_2$H$_4$

it is believed that the rest potential of the hydrazine system on platinised platinum in acid perchloric solutions is in fact a mixed potential and that the differing rates of adsorption for the conflicting or subsequent reactions cause the potential of the electrode to change in a manner corresponding to the changes in surface coverage of the various species. This is reflected in the results shown in Figure 6.

## CONCLUSIONS

From the examination of interfacial characteristics of smooth platinum and platinised platinum in acid and alkaline hydrazine solutions in the presence of hydrazine reactions, is suggested that the rate controlling reaction is not primarily via a low pressure hydrogen type of oxidation but rather of a sequential oxidation of hydrazine radicals and products of the initial oxidation of hydrazine. The state of the electrode surface plays a considerable rôle in which mechanism becomes controlling and it is probable that the reactions on smooth platinum are not the same as those on platinised platinum. On a platinised platinum surface with suitable conditions of acid and hydrazine concentrations, the reversible hydrogen reaction can have some effect. It is postulated that the electrode surface may be covered by a strongly adsorbed species resulting from the initial oxidation of the hydrazine molecule.

# The Complex Impedance of Smooth Platinum in Perchloric Acid

In order to examine the effects of fuel cell reaction products upon the electrode-electrolyte interface, reliable data was needed on the characteristics of this interface with conditions most nearly clean and pure as possible. To this end, it was decided to examine the impedance of smooth platinum in perchlorate solution. The perchlorate ion is non specifically adsorbed on most metal electrodes and certainly less than any other anion. Grahame[7] had previously attempted to obtain the reproducibility of impedance data on platinum that he obtained on mercury but indicated that the pre-treatment of the electrode was too critical and that a considerable frequency dispersion was obtained, indicating either the presence of a Faradaic process or adsorption effects, so that the capacitative fraction of the impedance was not solely due to orientation of solvated ions at the electrode surface.

## EXPERIMENTAL

The platinum electrodes were prepared as flame smoothed coherent spheres from platinum wire. The electrodes were sealed into soda glass and soaked in aqua regia. Following this, the electrodes were soaked in pre-purified water for two days and concentrated sodium hydroxide solution for six hours. Finally, the electrodes were soaked in 50% hydrazine solution for one hour, washed with aerated pre-purified water and stored in de-aerated pre-purified water. Solution of perchloric acid and sodium perchlorate were prepared of the required molarity and electrolyzed for 24 hours to remove traces of heavy metals. Finally on assembly of the cell and solutions, purified nitrogen was bubbled for one hour to exclude carbon dioxide and oxygen.

Impedance data were obtained using a series combination of capacitance and resistance at various frequencies, according to established practice.

## Results

The series capacitative fractions of the complex impedances of a smooth platinum electrode in, 0.1$\underline{N}$ and 0.1$\underline{N}$ perchloric acids are shown in Figure 7. The values obtained at only two frequencies of 500 cps and 5 kcps are shown. At 5 kcps the contribution of a Faradaic process to the double layer capacity is negligable.

At potentials more negative than the saturated calomel electrode (S.C.E.) can be seen the contribution of the Faradaic admittance due to the reversible hydrogen reaction. As is expected, as the pH increases the reversible hydrogen potential shifts to more negative potentials and hence the contribution to the impedance at -.2V vs. S.C.E. decreases.

A frequency dispersion between the values obtained at 500 cps and 5 kcps is observed throughout the whole potential range, although the dispersion obtained at the start of pure oxide formation remains constant throughout the oxide forming range, indicating that the only process significantly changing is the increase in surface areas due to expansion of the platinum lattice to accomodate the oxygen atoms. The double layer capacity values obtained at the start of oxide formation and at 5 kcps are extremely reproducible as shown in Figure 7 at the minimum around +.8V vs. S.C.E. whilst the shift of this minimum of about 70 mV with unity change of pH is evident. The minimum is not well enough defined to be more precise than this, other than showing the trend. It will be shown later that addition of carbon monoxide facilitates location of the start of oxide formation.
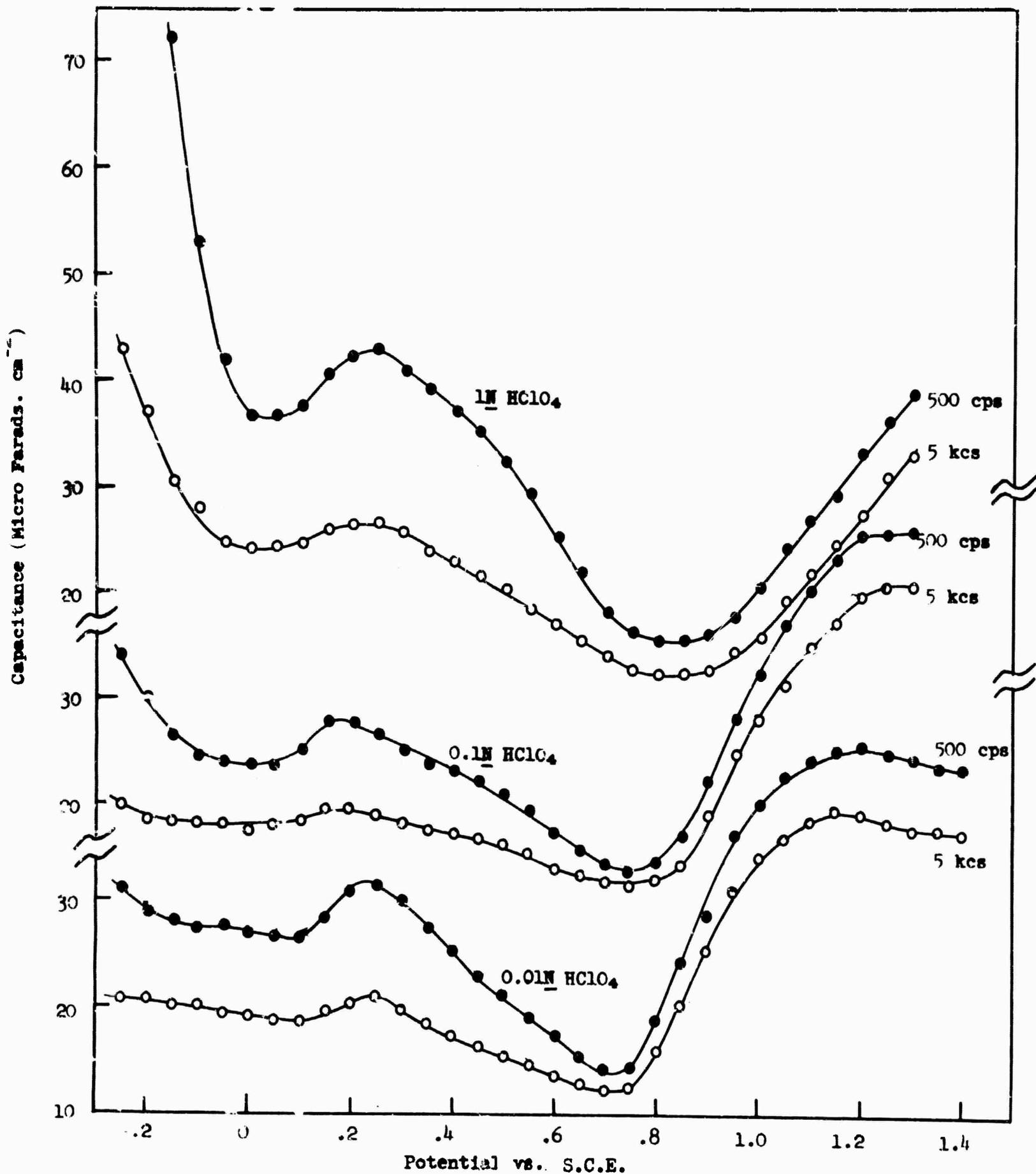
Figure 7. Double Layer Capacitance of smooth Platinum with varying pH.

The small hump in the capacity curves appeared to be insensitive to changes in pH and was quite reproducible at 5 kcps, although at 500 cps the magnitude changed between different platinum electrodes used. It was thought that this might be due to orientation of the water at the electrode surface similar to that shown on mercury and [8] that if so, then the magnitude of the hump should be thermally sensitive and minimizing at higher temperatures. Accordingly a series of capacity determinations were undertaken in 1N perchloric acid and with variation of the temperature of the solution between 5°C and 50°C. The results are shown in Figure 8. It cannot be said that over this temperature range there is a major significant difference in the capacities obtained, as the experimental error was probably as great as any change. If this hump is due to orientation of water, then it is bound much more strongly to the platinum surface that is the similar bonding to a mercury surface. Further work would be needed to resolve this point which is of only cursory interest at the present time.

Lastly, as co-workers in this laboratory had shown the large influence of chloride ions upon methanol fuel cell reactions in perchloric acid an examination of the effect of traces of chloride ion on the double layer capacity and the corresponding frequency dispersion were examined. Typical results are shown in Figure 9. The most dramatic effect is the increase in the capacity in the reversible hydrogen region. Here the magnitude at -.2V vs. S.C.E. approaches ten times that observed in the absence of the trace of chloride. The double layer rapidly decreases as the potential is increased until at +.5V vs. S.C.E. the value coincides with those obtained in the absence of chloride up to the start of oxide formation. Interference with the lattice expansion is then
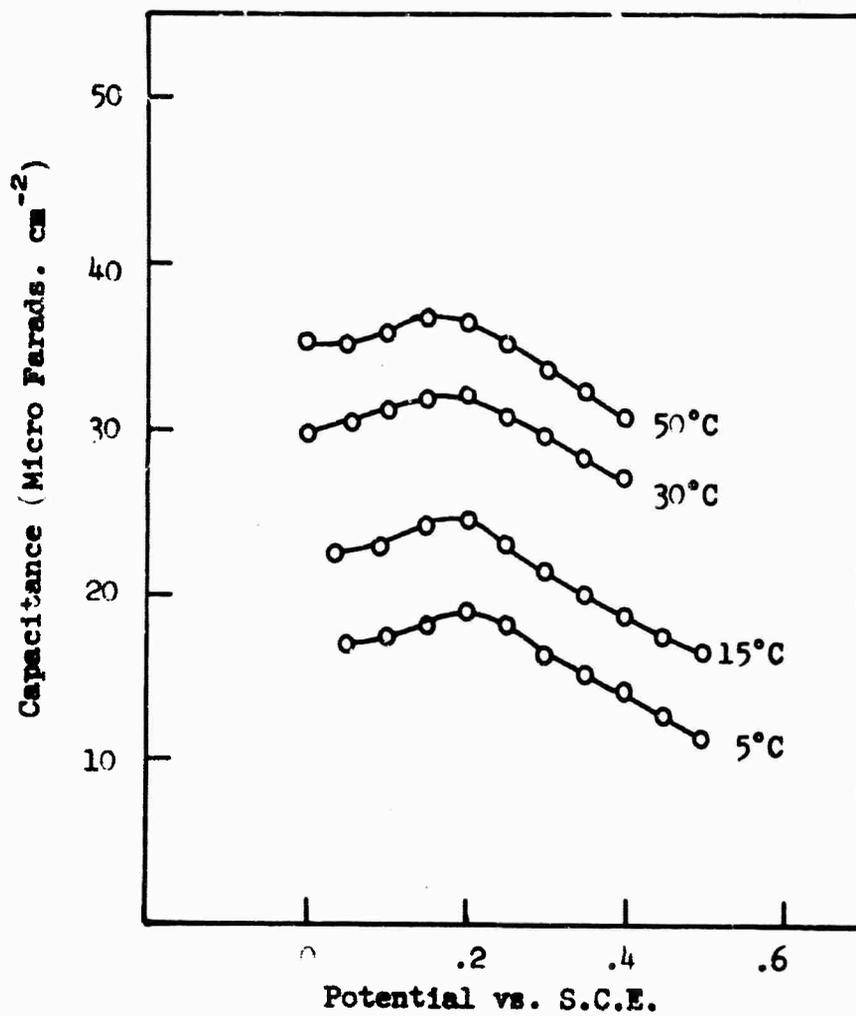
**Figure 8.** Double Layer Capacity of Smooth Platinum in 1N HClO₄ Measured at 5 kcs. Temperature Variation.
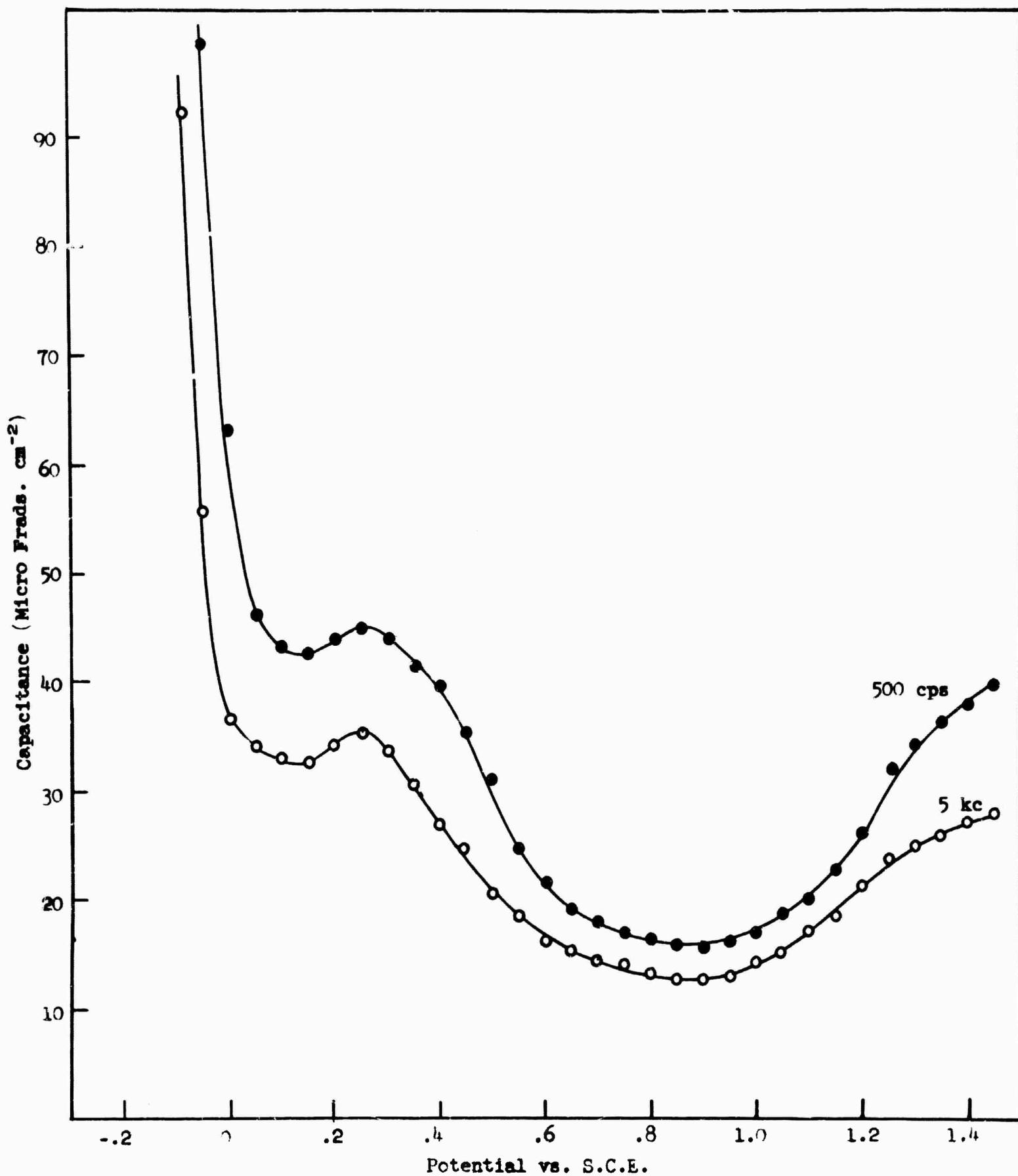
Figure 9. Double Layer Capacitance of Smooth Platinum in $1\underline{N}$ $HClO_4$ Containing $0.05\underline{N}$ Chloride Ion.

evident on further incre se of potential, as the surface area increase

is not so marked and frequency dispersion increases abov 1.2V vs. S.C.E.

due to oxidation of the chloride ion at the electrode surface.[9]

## Effect of the Reversible Hydrogen Reaction

The mechanism for the oxidation of hydrogen and the converse

reaction, the evolution of hydrogen at platinum electrodes has occupied

much of the literature. A recent review by Frumkin has examined the[10]

most recent work on a series of electrode materials. For the reversible

hydrogen reaction to occur on platinum, it would appear that the surface

of the electrode should have a significant coverage of adsorbed hydro-

gen, whilst Shuldiner shows that for solution of hydrogen, the rate[11]

limiting step is the slow combination of hydrogen atoms adsorbed on

the electrode surface.

For interpretation of the capacity data on smooth platinum

in acid solutions and the influence of organic electrode reactions, it

is required that data be obtained for the impedance effects of the

reversible hydrogen reaction itself. An examination of the double layer

capacity of a smooth platinum electrode using an impedance technique

was originally carried out by Dolin and Ershler on a frequency range[12]

of 10 to 6,750 cps. Under these conditions a considerable "pseudo"

capacity due to the Faradaic admittance of the hydrogen system was

observed. In addition, additional peaks at more positive potentials

than the reversible hydrogen potential have been observed, these[13]

being attributed to removal of "loosely" bound hydrogen atoms and

"strongly" bound hydrogen atoms at the metal surface.

The surface coverage of adsorbed hydrogen at a given potential is given by the "pseudo" capacity of the electrode such that

$$C_2 = - \text{const.} \frac{\partial \, C_H}{\partial \, E} \qquad (11)$$

where the "pseudo" capacity $C_2$ is defined as the deviation of the experimental double layer capacity from the true double layer capacity due to the Faradaic admittance. The value of the true double layer capacity is approached at high frequencies when the effect of the Faradaic process is minimised.

In Figure 10 is shown the capacitative component of the electrode impedance as a function of frequency and potential. These results were obtained in a 1N perchloric acid solution at 25°C saturated with hydrogen. The impedance was measured as a series combination of resistance and capacitance, no attempt being made to extract the ohmic resistance of the solution or the true double layer capacity. The "pseudo" capacity for the hydrogen reaction is quite apparent as are the secondary and tertiary peaks at more positive potentials. At +0,5V vs. NHE the frequency dispersion has greatly decreased, indicating that the phase changes in the A.C. signal produced by the hydrogen reaction and adjucts have little or no effect. These results are similar to those of Breiter,[13] who indicated that the surface coverage of adsorbed hydrogen on platinum was zero at +0.3V vs. NHE.

Much of the capacity dispersion shown in Figure 10 is attributed to the diffusional impedance of the hydrogen from the bulk of the solution to the electrode surface. It follows that the surface concentration of hydrogen at an electrode of a given potential in solutions of the same pH will be the same and therefore the difference between the effects of
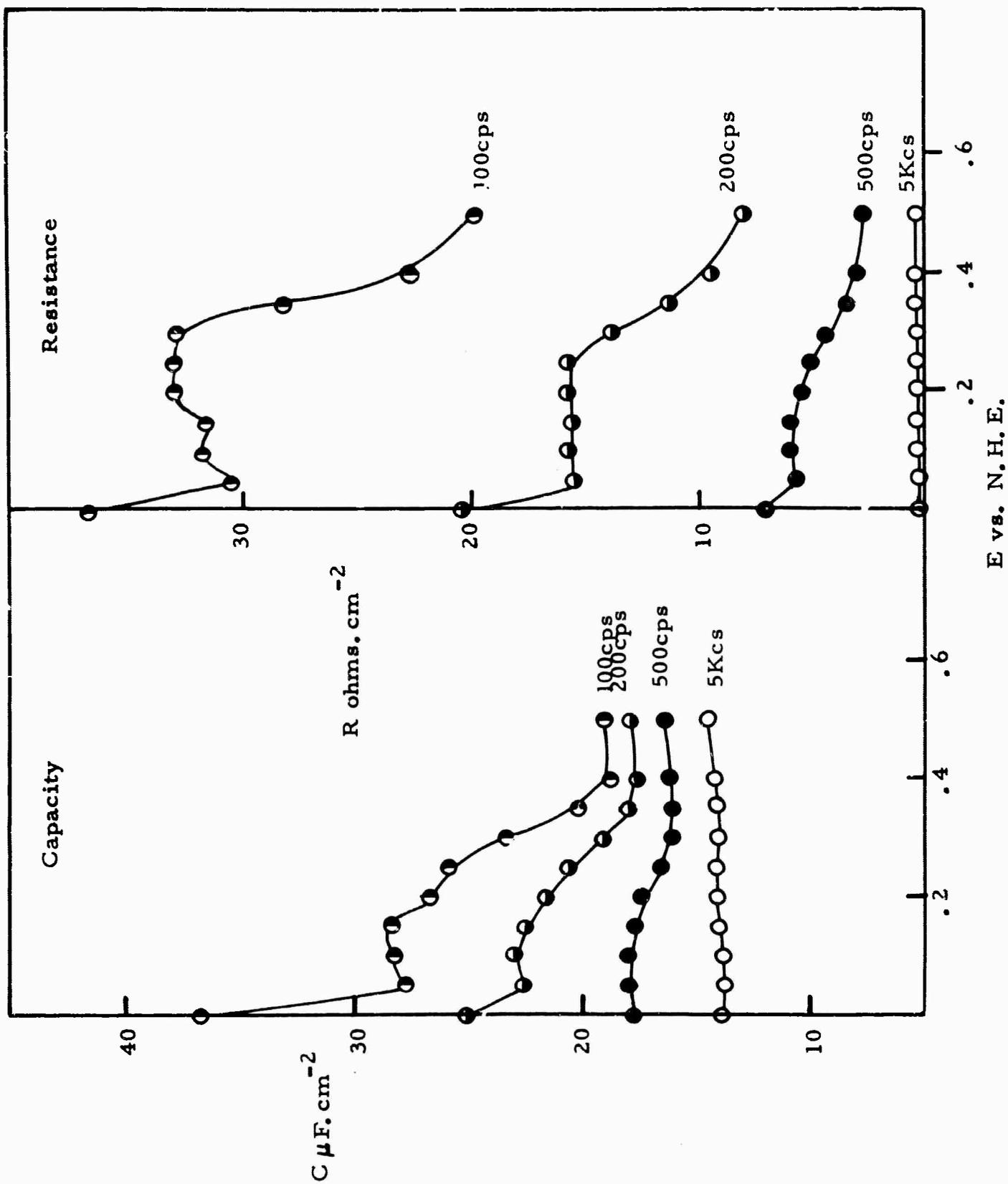
Figure 10. Impedance of $H_2$ on Pt in 1 N HClO$_4$

dispersion of the capacitative fraction of the impedance in Figure 10 and 7 are meaningful. From Figure 10 it is apparent that the effect of adsorbed hydrogen is negligible above +.1V vs. S.C.E.

An examination of the quantity of hydrogen adsorbed at a platinum surface has been carried out by Frumkin[14] using a charging technique. In this manner, the manner of coulombs required to produce a given potential change has been correlated to the amount of hydrogen present on the electrode surface at that potential. With this method, only the readily removable hydrogen will be observed and it is debatable whether or not the strongly bound hydrogen will remain. Indeed, the hydrogen may be physically trapped at the surface interstitially on by formation of a compound Pt $H_x$. In addition, little considerations have been given to the effects of diffusion of the hydrogen out of solid solution in the electrode to react at the electrode surface. As hydrogen has a significant solubility in platinum a real concentration gradient would be formed on removal of "surface" hydrogen.

Sawyer and Seo[15], using voltammetry have clarified the presence of peaks in the i-v curves for the oxidation of hydrogen on platinum but correlation of these peaks to the catalytic power of the electrode surface has not been successful. No effects on the current density can be correlated to the secondary and tertiary capacity peaks shown in Figure 10. Also in the presence of hydrogen in the bulk of the solution, the hump in the capacity curves at +.2V vs. S.C.E. shown in Figure 7 does not appear.

## Oxidation of Carbon Monoxi<u>de on Platinum in Perchloric Acid</u>

When the electrochemical oxidation of an organic fuel is considered, the electrochemical oxidation steps are no longer simple as for rapid inorganic ions but proceed in a sequential manner with formation and subsequent oxidation of many intermediates. Whether or not the intermediate formed is stable enough to diffuse away from the electrode, is a function of its stability and energy of bonding to the electrode surface. Ideally for all hydrocarbon fuels, the final product of the react.on is carbon dioxide, irrespective whether the starting materials is methanol or propane and one might consider therefore that if the ultimiate reaction step is desorption of the carbon dioxide, then the penultimate step would be oxidation of either carbon monoxide - CO or a carboxyl group - COOH at the electrode surface. The oxidation of carbon monoxide and its relation to the methanol reaction for example, was therefore undertaken.

Some previous work specifically examining the oxidation of carbon monoxide on platinum was performed by Gilman,[16] who concluded that carbon monoxide existed at the platinum surface in two isomeric forms, one linear and the other bridged with regard to surface bonding. This data however is concerned with potentials where the electrode surface is covered with oxide and very little information can be gleaned about useful potential regions, for example within +0.4 vs. normal hydrogen electrode. (N.H.E.).Giner,[17] on the other hand examined the reduction reaction of carbon dioxide and observed a peak using cyclic voltametry and called this "reduced carbon dioxide" although he did not differentiate between carbon monoxide or carboxyl. The peak is

observed when both methanol and formic acid are oxidized, lending

credance to a partial oxidation mechanism via an intermediate from

the carboxyl group.

In the subsequent work presented here, an examination of

the interfacial characteristics of smooth platinum when reacting

with carbon monoxide in acid solution was carried out.

## Experimental

Tank Carbon monoxide was purified by passing through Linde

molecular sieve 5A, specifically to remove iron carbonyl which is

always present in significant quantities. Normal gas train procedures

were then used prior to passage through the cell. Experimental deter-

minations of voltammetric characteristics were performed on a slow

sweep apparatus developed by W. H. Smart. Under these conditions of

sweep $0.2V \, min^{-1}$, sufficient time was allowed for any oxide reactions

to come to a situation approaching steady state. The complex impedance

of the double layer was examined using the Wien bridge described in

Appendix II.

## Results

The voltammetric characteristics of carbon monoxide on smooth

platinum are shown in Figure 11. The values obtained with quiescent

solution conditions and vigorous bubbling with carbon monoxide are shown

superimposed. It is evident that diffusion of carbon monoxide to the

electrode makes little or no effect below potentials of +1.1V vs. N.H.E.

and even at +1.2V vs. N.H.E. the effect is by no means considerable. In

this manner we may discount any significant diffusion control of the
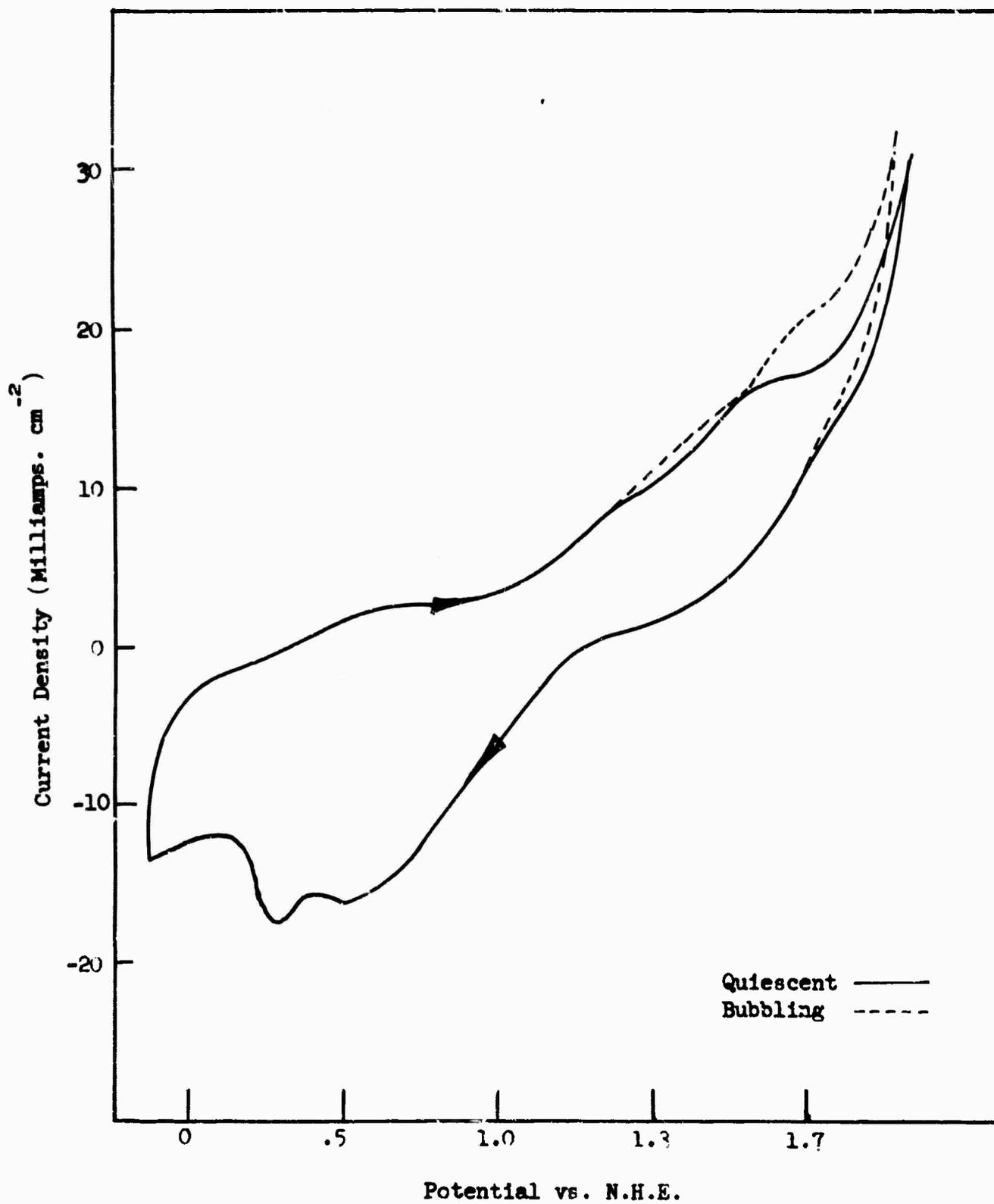
Figure 11. Voltammetric Characteristics of Carbon Monoxide Saturated
1N HClO₄ on Smooth Platinum.

electrode reaction. The other very interesting result seen in Figure 11
is the suppresion of the reversible hydrogen reaction by the carbon mon-
oxide, for the cathodic liberation of hydrogen does not occur until very
large (for hydrogen) over-potentials are reached of about -.100 mV vs.
N.H.E. This blocking or "poisoning" of the hydrogen evolution reaction
can only be ascribed to site saturation by adsorbed carbon monoxide
molecules and hydrogen evolution cannot occur until the carbon monoxide
is removed either bv reduction to another species or slow desorption,
which would be unlikely under these conditions. The affinity of carbon
monoxide for platinum is well known from gas phase data where there is
a large body of work devoted to the adsorption of carbon monoxide on
platinum. In aqueous solutions, similar conditions would be expected
although the physical situation existing is dependent on the ability
of the carbon monoxide to desorb preferentially the adsorbed water
molecules at the electrode-electrolyte interface.

The interference of carbon monoxide with the hydrogen reaction
is shown most clearly in the double layer capacitance data shown in
Figure 12. Here the double layer capacities of smooth platinum in carbon
monoxide saturated solutions with varying perchloric acid concentrations
are shown. These data may be compared directly with those presented in
Figure 7. In all cases of solutions of 1.0, 0.1, 0.01$\underline{N}$ HClO$_4$ saturated
with carbon monoxide, the double layer capacity measured at 5 kcps is
appreciably lower than the values obtained in the absence of carbon
monoxide. In fact, a remarkable consistancy of the values for the double
layer capacity is observed from potentials of -.2V vs. S.C. E. to +.7V vs.
S.C.E. with little or no variation. At the most negative potentials
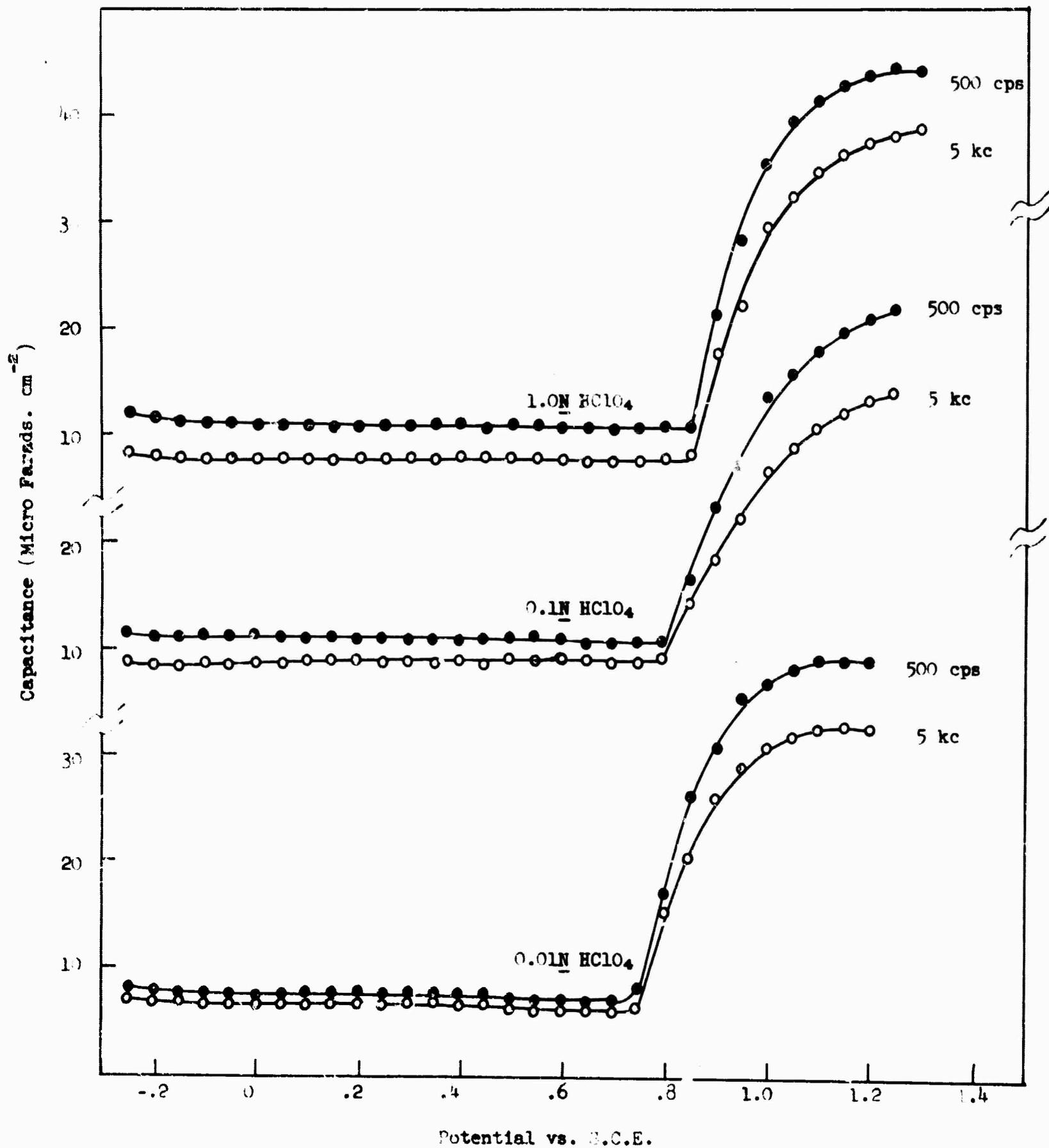
Figure 12. Double Layer Capacitance of Smooth Platinum in Carbon Monoxide Saturated Solutions of Varying pH.

(-.25V vs. S.C. E.) no evidence can be seen for the "pseudo" capacity
due to the reversible hydrogen reaction as the carbon monoxide has
blocked the reaction at this potential.

At potentials where significant formation of surface oxide
begins, a sharp break in the double layer capacity occurs, specifically
characterising the potential of oxide film formation and the double
layer capacities revert to those values for the platinum oxide in the
absence of carbon monoxide. Here then, the strongly bound carbon mon-
oxide at the electrode surface is catalytically oxidized via the platinum
oxide to give carbon dioxide. It is in this region that slight diffus-
ional effects were observed from the voltammetric sweeps.

The potential of oxide formation is clearly indicated
by the changes in the double layer capacity and the potential changes
by 60 mV per tenfold change in acid concentration (approx. each pH unit).
No evidence can be seen for significant oxide formation below these
potentials although it may be reasoned that less active forms of oxide
e.g. hydroxide occuring at low potentials may not be sufficiently
active to oxidize the carbon monoxide at the surface.

Examining the frequency dispersion of the double layer capacity
between 5 kcps and 500 cps in Figure 12 it is shown that the dispersion
is very small, indeed, such a small dispersion has not previously been
observed on solid electrodes. Only the mercury electrode
in the inert salt solution with absence of a Faradaic reaction and
adsorption has exhibited frequency independence for double layer values.

Consideration of the various analogue circuit components at
the electrode interface may be used to explain the effect of the carbon
monoxide at the surface. On mercury in an inert salt solution with

absence of a Faradaic reaction and adsorption, the impedance is composed
of a series resistance $R_o$ due to the ohmic resistance of the solution
and capacitance $C_{dl}$ due to the orientation of ions at the electrode
surface to produce the double layer.

$$e.g. \quad -| |-\!\!-\!\!\!\bigwedge\!\!\bigwedge\!\!\!-\!\!- \qquad (12)$$
$$\phantom{e.g. \quad} C_{dl} \qquad R_o$$

In the presence of a rapid reversible electrode reaction, the double
layer capacity is effectively bypassed by a subsidiary impedance com-
posed of an impedance due to diffusion of species to and from the elec-
trode (Warburg $R_w$ & $C_w$) and an ohmic resistance $R_a$ due to the electron
transfer controlling step in the reaction.

$$e.g. \qquad (13)$$

where the bridge element contains $R_a$, $C_w$, $R_w$ on top, $C_{dl}$ below, and $R_o$ in series.
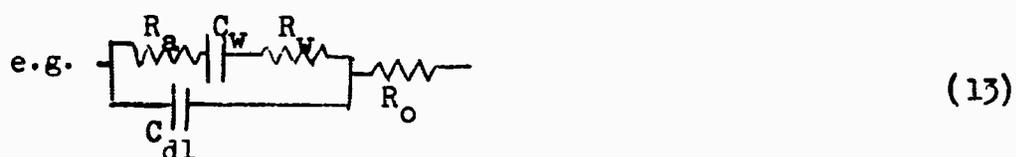
Conditions for extraction of the Warburg impedance and determination of
the electron transfer resistance are known.[18]

When the electrode reaction is slow Ra $\longrightarrow \infty$ and there is no
diffusional impedance. In addition, when preferential adsorption of
some species occurs that is not affected by the sinusoidal perturbation
of the voltage at the electrode, then the analogue appears as two capac-
ities in series $C_{dl}$ and $C_{adsorption}$ together with the ohmic resistance
of the solution.

$$e.g. \quad -\!\!-| |-\!\!-\!\!| |-\!\!-\!\!\bigwedge\!\!\!-\!\!- \qquad (14)$$
$$\phantom{e.g. \quad} C_{ads} \qquad C_{dl} \qquad Ro$$

If this condition is so and Ra $\longrightarrow \infty$, then a similar circumstance
would be obtained analogous to the pure mercury condition and little or no
frequency dispersion observed, as the frequency dispersion is due to the

complex impedance network set up at the electrode, owing to the bypass of the double layer capacity by the Faradaic reaction. $(Ra + R_w + C_w)$ The maximum frequency dispersion is then obtained when $Ra \longrightarrow 0$ as $R_w = \dfrac{1}{\omega C_w}$

Experimentally, there is further evidence that the carbon is covering the surface by the reasoning that the total capacitance of two individual capacitors in series obeys a reciprocal relation.

$$\frac{1}{C_{apparent}} = \frac{1}{C_{dl}} + \frac{1}{C_{ads}}$$  (15)

If $C_{ads} \approx C_{dl}$, then $C_{app} \approx \dfrac{C_{dl}}{2}$; which is approximately the situation observed by comparing the capacitance values in Figure 7 and 12. If the above equation holds true at all potentials between -.2v and +.7v vs. S.C.E. then it would be expected that the capacitance values shown in Figure 12 should show some variation. As this is not the case, then the capacitance variations due to the reversible hydrogen reaction, platinum hydride and hydroxide are blocked by the carbon monoxide. In addition the sites for water orientation are also blocked and it may be that the aqueous structure at the electrode surface is altered significantly.

On the basis of the work presented here it is not possible to substantiate the conclusion obtained by Gilman,[16] especially as the electrode has significant coverage of carbon monoxide at potentials up to +1.2V vs. S.C.E.

## Oxidation of Methanol, Formic Acid and Formaldehyde

Solutions of $1\underline{M}$ methanol, $1\underline{M}$ formic acid and $1\underline{M}$ formaldehyde, each in $1\underline{M}$ perchloric acid were oxidized at a smooth platinum electrode and the double layer capacitance examined in each instance and the results are shown in Figures 13, 14, and 15 respectively.

The general shapes and magnitudes of the capacitance curves are akin to those obtained for smooth platinum in the absence of any electrode reaction. In each case the "pseudo" capacity due to the reversible hydrogen reaction is clearly shown as is the hump in the curves at +.2V vs. S.C.E., although it is more pronounced in the methanol and formic acid oxidation than in the formaldehyde case. In no circumstance is there evidence that a carbon monoxide type of adsorbed film is affecting the capacitance. If the carbon monoxide was produced as an intermediate of the methanol reaction, it would be evident from the impedance data that the strongly absorbed species was present. The only situation whereby the carbon monoxide could have no effect would be if it was removed at a rate greater than its production - a postulate that is not borne out by the voltammetric behavior.

The mechanism of oxidation of the carbon monoxide is essentially via platinum oxide or hydroxide formation below 1.24V vs. N.H.E.

$$Pt + 2H_2O \longrightarrow Pt(OH)_2 + 2H^+ + 2e^- \tag{16}$$

$$Pt(OH)_2 + 2CO \longrightarrow 2CO_2 + Pt + 2H^+ + 2e^- \tag{17}$$
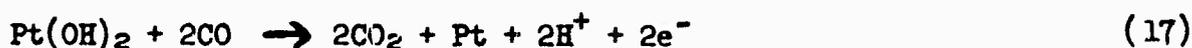
For the oxidation of methanol, the primary oxidation path is via formic acid and then to carbon dioxide.

$$CH_3OH + H_2O \longrightarrow HCOOH + 4H^+ + 4e^- \tag{18}$$

$$HCOOH \longrightarrow CO_2 + 2H^+ + 2e^- \tag{19}$$

The competition for formation of formaldehyde occurs with the first step.
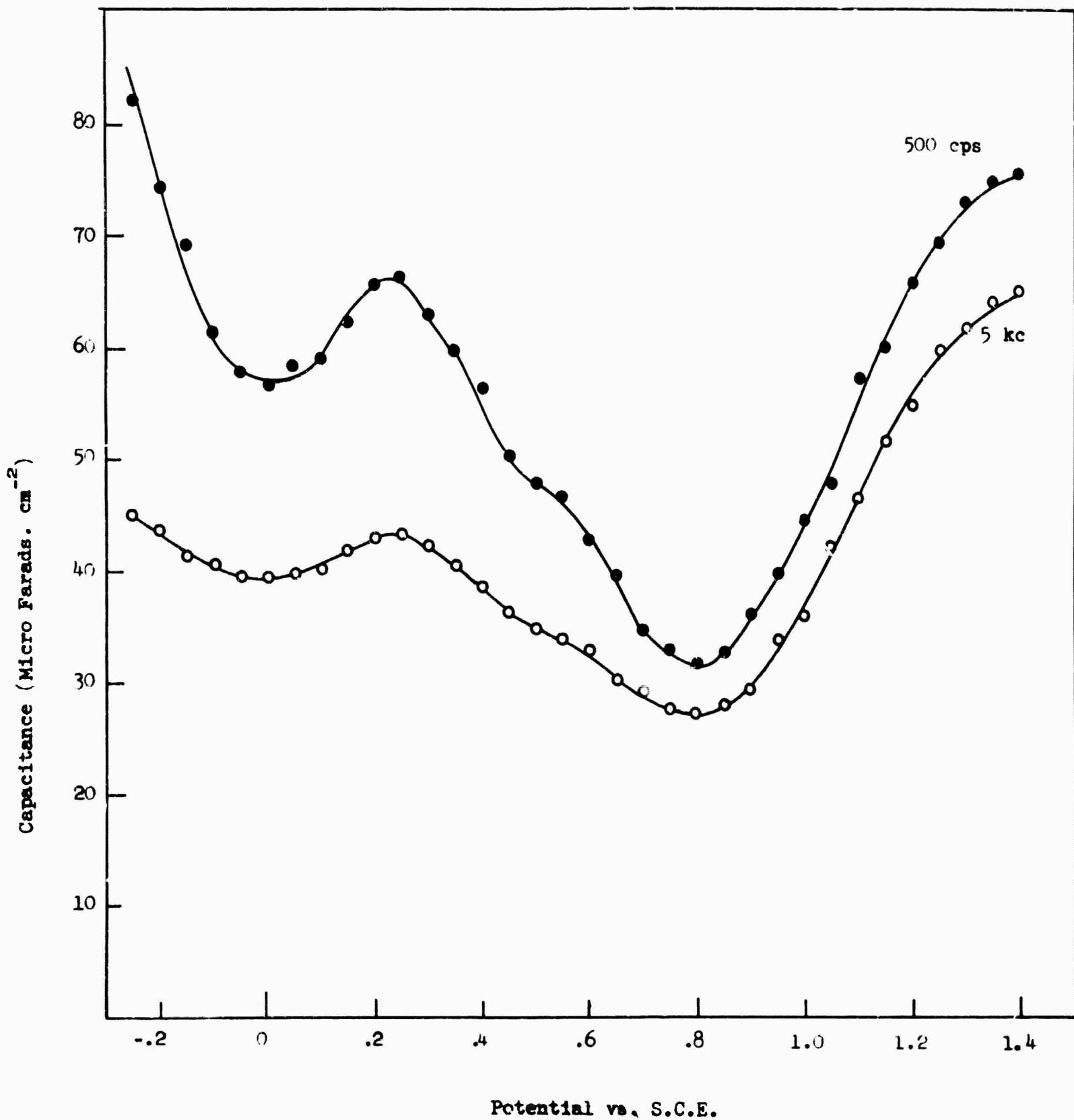
Figure 13. Double Layer Capacitance of 1M Methanol in 1M HClO₄ on Smooth Platinum.
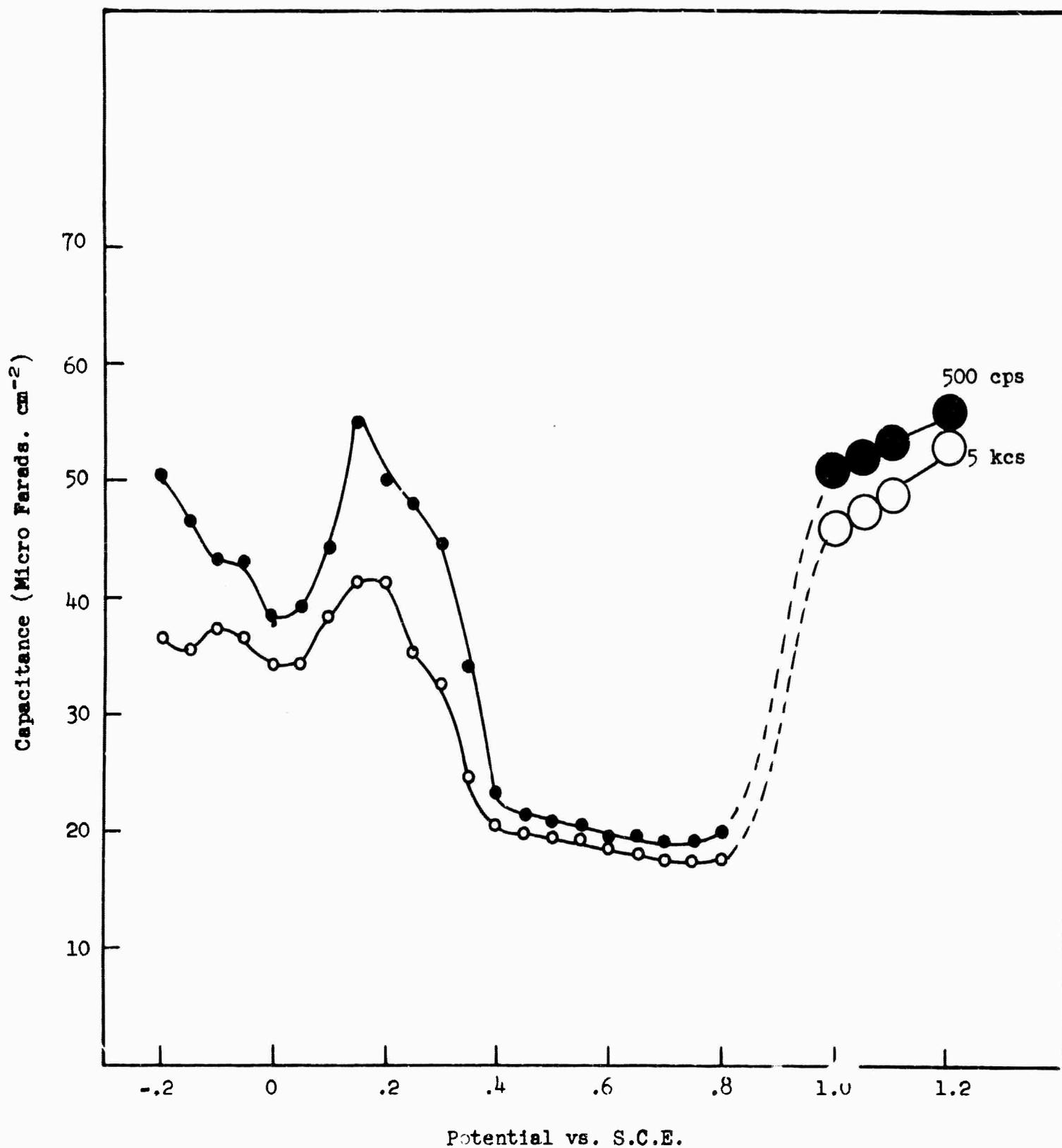
Figure 14

Double Layer Capacitance of 1M̲ Formic Acid

in 1N̲ HClO$_4$ on Smooth Platinum
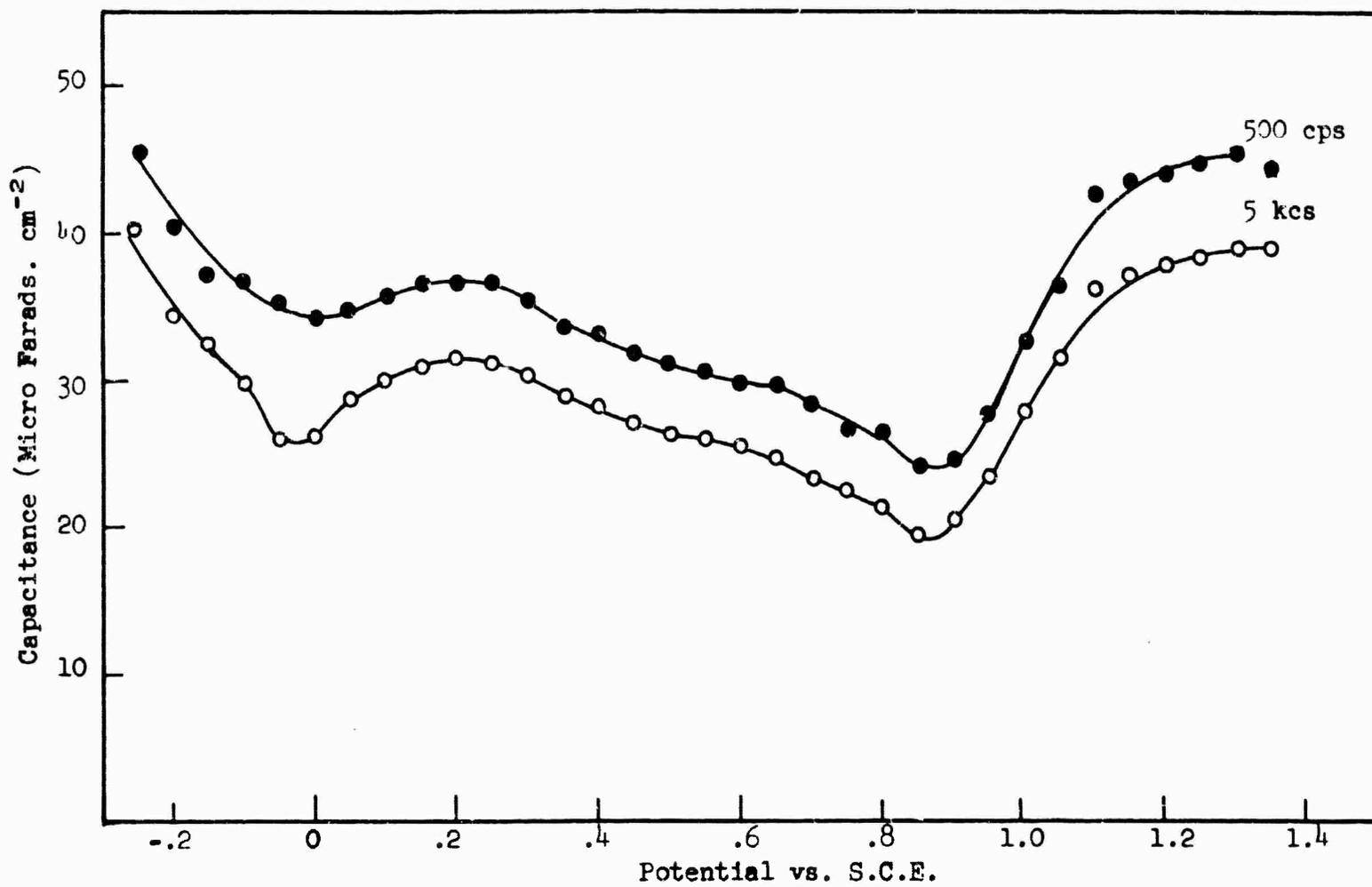
Figure 15    Double Layer Capacitance of 1M Formaldehyde in

1N HClO₄ on Smooth Platinum

## Thin Film Chronopotentiometry

To obtain a very high electrode area to volume of solution ratio, the dimensions of the electrode and solution volume must be very closely defined. This was carried out by taking a thin sheet of plastic film and cutting a circular hole in it. A flat platinum sheet electrode was placed on one side of the plastic film covering the hole completely, whilst a flat inert support covered the opposite side of the film. Thus the hole cut out of the film was enclosed on both sides giving a defined volume and the apparent surface area of the electrode became that of the cross sectional area of the hole in the film. Provision was then made for electrical connection to the solution in the cell for a reference electrode and for a polarising counter electrode. This was made possible by drilling two small holes through the support to make connection to the edges of the disc of solution. The cell is showed in Figure 1A.

Fabrication of the retaining plates to sandwich the electrode and film together was carried out by machining blocks of "Lucite". The assembly was held together by four nylon screws and the film or "gasket" for defining the volume of solution was prepared from duPont "FEP" plastic. Two thicknesses of film were used, these being 0.010 inch and 0.005 inch, giving different cell volumes. DuPont "Teflon" was used initially as the "gasket" material, but proved to be too rigid and allowed seepage of electrolyte out of the electrode compartment. In this manner, the results obtained using a "Teflon" gasket indicated a higher apparent concentration of electroactive material in the volume of solution.

The constant current generator was made by taking a regulated D. C. Voltage from a Harrison Laboratories 855B voltage generator and placing in the output, a series combination of 1 Megohm variable potentiometer, the cell and a Pye "Scalamp" glavanometer to measure the current. A small relay was inserted into the circuit to enable rapid switching off, on and reversing of the current.

The electrochemical potential between the test electrode in the cell and a reference electrode was recorded on a Varian G-11 recorder using a 100 K potentiometer to give a one volt scan deflection on the recorder. This cell is similar to that of Anson and Christansen[6] who examined electrode characteristics in thin layers of solution.

## Theory

For a reversible reaction, the potential of the electrode in a solution will be governed by the ratio of the concentrations of the products to the reactants in the solution -- the well known Nernst equation.

$$E = \text{const.} + \frac{RT}{nF} \ln \frac{C_{\text{oxidised}}}{C_{\text{reduced}}} \tag{20}$$

(the concentration may be approximated for the activity).

On passage of a very small current, such that the concentration in the thin film of solution changes very slowly and no concentration gradients are set up, then the potential of the test electrode will follow the Nernst dependence of the concentration in the cell. At the point of total oxidation or reduction of the species in the solution (depending on the direction of current flow) the potential will rapidly change to another reaction capable of facilitating the passage of the required constant current.

Let us assume that the species in the cell is being reduced.

When total conversion of the oxidized form to the reduced form occurs, the potential is such that the concentration of oxidized species at the electrode surface tends to zero. We may then apply an equation to relate the potential of the electrode to the ratio of the concentration of the electroactive species in the film, expressing this as a function of time. Hence

$$E = \text{cont.} + \frac{RT}{nF} \ln \frac{t}{\mathcal{T}\text{-}t} \tag{21}$$

In the equation above, $\mathcal{T}$ is the time required to obtain total reduction of the species and t is any intermediate time, provided the initial concentration of the reduced species was zero.

For a reaction where the surface of the electrode is electroactive to such an extent that it forms part of a reversible couple, then the equation would take the form

$$E = \text{cont.} + \frac{RT}{nF} \ln \frac{\mathcal{T}}{\mathcal{T}\text{-}t} \tag{22}$$

Again assuming that the species in the cell is being reduced and that the initial concentration of the reduced form in the solution is zero. This equation applies when reduction of the oxidised form gives an adsorbed film of constant concentration on the surface of the electrode metal itself.

Then $\mathcal{T}$ is again the time of total reduction of the oxidised species within the cell and t is any intermediate time.

Knowing the volume of the solution, the concentration of the electroactive species in that solution, the current density and measuring the time for total conversion, then the number of coulombs required for the overall reaction was easily obtained.

## Examination of Characteristics of Electrode Reactions Using the Thin Film Technique.

As the Ferricyanide-Ferrocyanide couple is reversible at a platinum electrode with both oxidised and reduced species soluble in the solution, then this couple was considered best to test the apparatus. An equimolar mixture of potassium ferricyanide and potassium ferrocyanide was used with 1M potassium chloride as supporting electrolyte.

Chronopotentiograms obtained are shown in Figure 2A for both anodic and cathodic polarization at the same current density. Analyses of the curves according to equation (21) are shown in Figure 3A.

The slopes of the lines are

$$\frac{\Delta E}{\Delta \log \frac{t}{\tau - t}} = 2.303 \frac{RT}{nF} \tag{23}$$

A slope of 60 mV was obtained confirming a one electron reaction

$$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-} \tag{24}$$
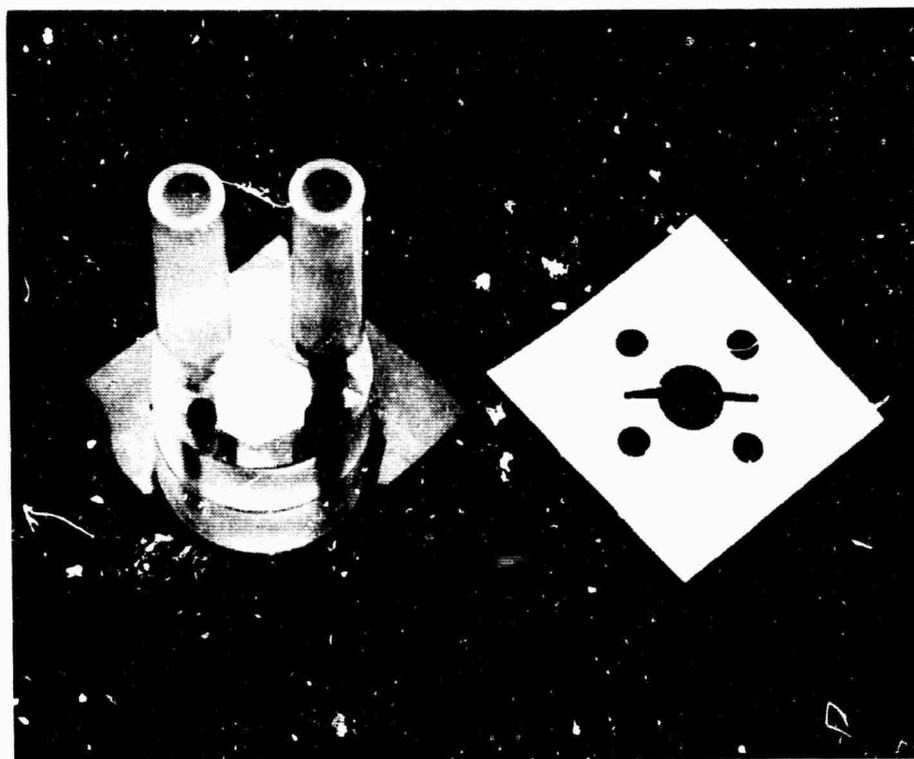
Figure 1A    Thin Film Cell

t
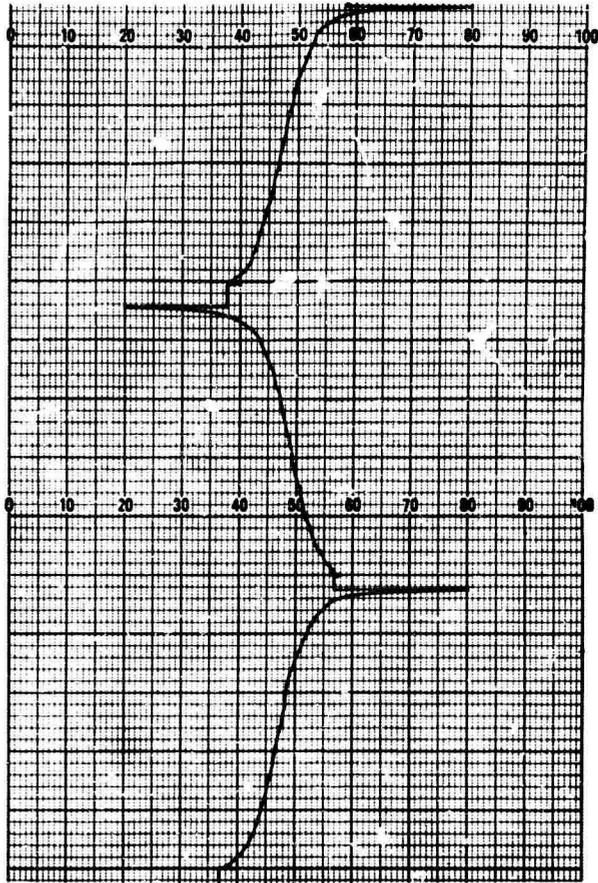
0      E vs. N. H. E.      1·0 V

Figure 2A   Ferricyanide-Ferrocyanide thin film chronopotentiogram

$\log \dfrac{t}{\tau - t}$
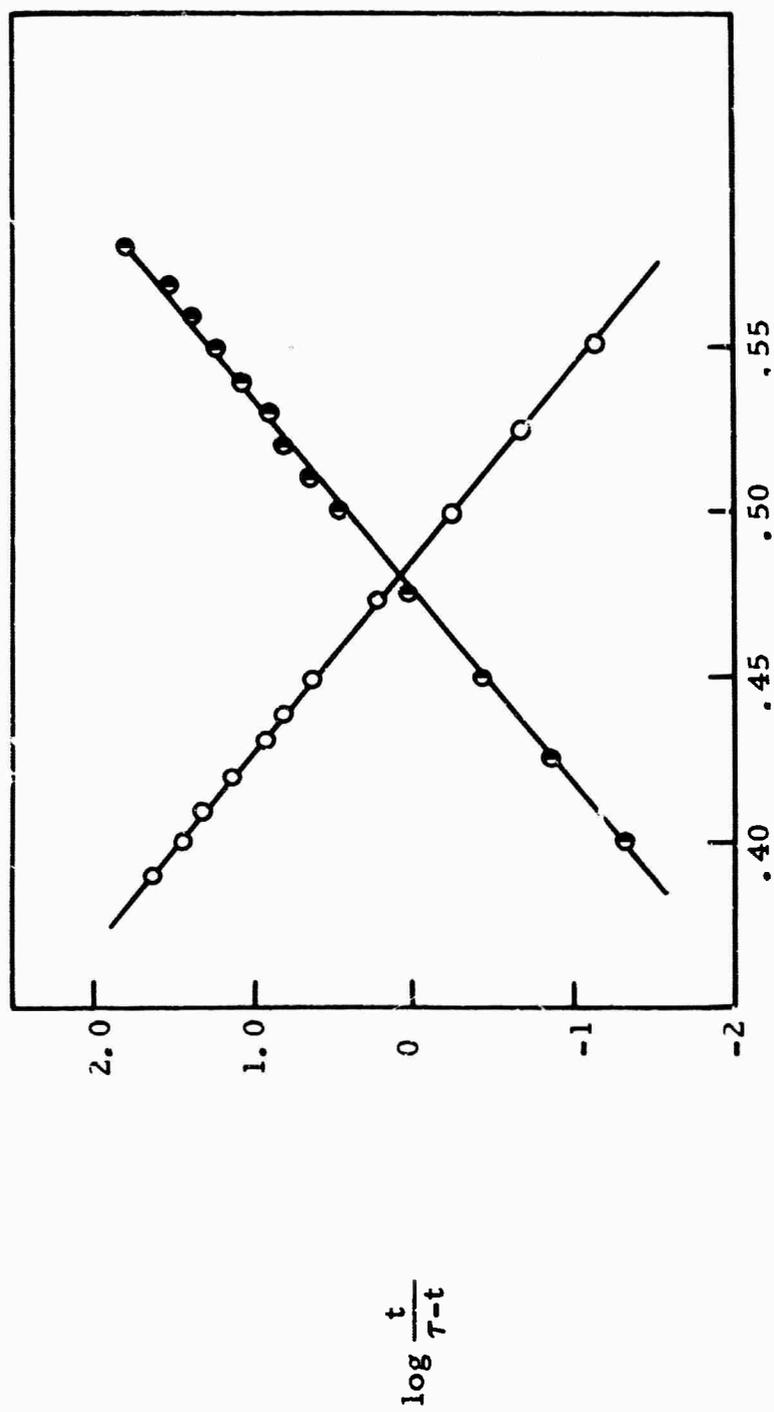
E vs. N.H.E.

Figure 3A  Ferrocyanide – Ferricyanide in 1 N KCl

## APPENDIX II

### Faradaic Impedance

To measure the impedance of the electrode surface, a Wien bridge system similar to that of Grahame[19] was constructed. The A.C. signal was generated with a Hewlett-Packard 204B oscillator feeding into a 1000:1 step down transformer. This signal was fed into the bridge network with sensitive ratio arms, the cell being inserted into one of the balancing arms of the bridge. The impedance was measured as a series resistance and capacitance in the opposite balancing arm. Balance detection was obtained by feeding the out of balance signal through a 122 Tektronix low level amplifier, followed by a 1232A General Radio tuned amplifier and null detector and finally into an oscilloscope. A circu_ diagram is shown in Figure 4A. Potential control was obtained by means of a small solid state potentiostat operating as a servo mechanism to balance the potential. Protection against leakage of the A.C. signal through the potentiostat or potentiometer circuit was accomplished by inserting a 68 Henry 600 mA choke in the circuit. The potentials of the test electrode were measured with a Rubicon potentiometer.

The two compartment cell was constructed from Pyrex glass with standard joint entry parts and greaseless taps to provide access between the two compartments. Provision was made to bubble purified gases through the cell, by incorporating a coarse glass sinter. The platinum test electrode was formed from a wire of pure platinum and sealed with soda glass. After sealing, the platinum wire was slowly melted in an oxygen-gas flame until a regular coherent sphere was produced. The counter A.C. electrode was a cylindrical platinum gauze, situated about the test electrode in such a manner that an even distribution for the field about the test electrode was obtained. The most important factor to be observed with the alternating

current counter electrode is that the surface area should be much greater than that of the test electrode, hence the impedance measured by the bridge is that of the smaller electrode.

Owing to the extremely low signal level to be detected at the balance point and remembering that the total maximum out of balance A.C. signal was only five millivolts, it was necessary to shield all electrical connections and to use co-axial cable.

The procedure for obtaining data with this apparatus entailed placing the test solution into the cell, passing a gas to either de-oxygenate or saturate with a given component, seal off the cell and allow quiescent conditions to obtain. Measurements of the impedance of the electrode in the presence and the absence of reactants at a series of frequencies and potentials were obtained as series combinations of re-sistance and capacitance.

When a small A.C. signal is passed through the electrode, electrolyte interface the effect upon the signal is exactly analogous to that obtained by passing through a network of resistors and capacitors in a strictly electronic sense. The double layer capacity appears as a pure capacitor and the resistance of the solution is purely ohmic. The sub-sidiary network due to the Faradaic electrode reaction behaves as an impedance in parallel with the double layer capacity and appears as a charge leak, often referred to as the Faradaic admittance. Owing to the sinusoidal nature of the perturbing signal, a diffusional impedance is obtained at the electrode and produces a phase change in the signal. This diffusional impedance is called the Warburg impedance and the function of the bridge circuit is to measure the total impedance of the electrode-electrolyte inter-face or the phase change of the signal. Solution of the impedance measure-ments may be carried out to extract the components using vectors[18] or algebraic transforms[20].

More specific details of the theory and practice of this technique have been given by Grahame[21] and a general review by Delahay[22].
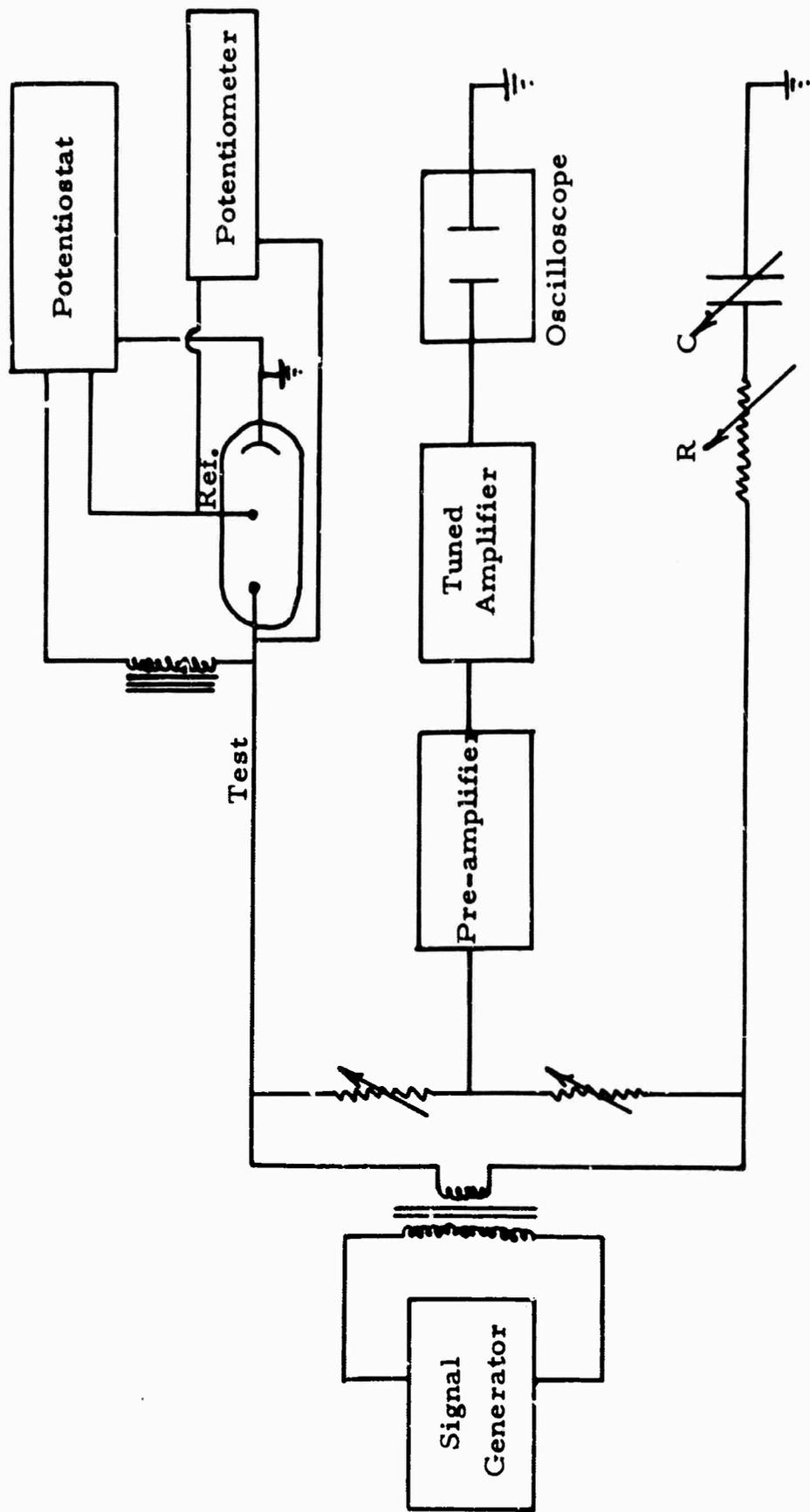
Figure 4A  Impedance Bridge

## APPENDIX III

### Coulostatic Pulse Technique on Ferricyanide-Ferrocyanide Systems

Several techniques now exist for determining kinetic rate
constants of electrode reactions, particularly for fast reversible re-
actions having a high exchange current at the rest potential. Many of
these techniques are now classical, these being the Faradaic impedance
method, current step and voltage step. All of these previous techniques
are influenced to some degree or another by the capacity of the double
layer at the electrode surface. For solid electrodes such as platinum,
the influence of surface oxides may drastically affect the measured
double layer capacitance so as to make solution or interpretation of the
results extremely difficult. In addition, specific adsorption of
species may interfere with the rate of the electron transfer.

A method recently presented to overcome some of these
difficulties is the coulostatic technique.[23] Here, the capacity of the
double layer is instantaneously charged with a rapid pulse and the
rate of leakage of this charge across the double layer shown to be a
measure of the rate of electron transfer for a rapid reaction.

### Experimental

The system examined was the potassium ferrocyanide-potassium
ferricyanide redox equilibrium. Solutions containing equal molarities
of potassium ferrocyanide and potassium ferricyanide were prepared
with a total ionic strength of 1.0 using potassium chloride as supporting
electrolyte.

The platinum electrode was prepared from fine platinum wire
(0.010" dia.) and sealed into soft glass. The protruding tip of the

platinum wire was then slowly melted in an oxy-gas flame until a
regular coherent sphere was produced. After cooling in the reducing
portion of the flame, the electrode was cleaned in aqua regia; nitric
acid; distilled water; dilute perchloric acid and finally left to soak
in distilled water for forty-eight hours before using.

The coulostat for producing the pulse was essentially that of
Delahay[24]; the circuit given in Figure 5A.

The battery was a Mallory ZM-9, giving about 1.35V. The
capacitor C was varied according to the size of the electrode, but for an
electrode having an apparent surface area of 0.1 sq. cm. then C=
0.004$\mu$F (MYLAR). For the counter electrode, a cylindrical platinum
gauze was used, surrounding the electrode and being carried through the
same electrode pre-treatment as the test electrode. In this manner,
the rest potentials of the two electrodes were readily obtained to
within 0.1 mV of each other. The potential signals were fed into a
Tektronix "D" differential D. C. amplifier and displayed on a Tektronix
551 oscilloscope. The relay comprised a break-before-make mercury
wetted reed (Clare HGS 5008) and total absence of contact bounce was
observed. All contacts from the pulsing device to the cell were
co-axial shielded and as short as possible to minimize "ringing".

Finally, the solutions were purged with purified nitrogen
prior to any determination of kinetic parameters.

The change of the electronic potential of the test electrode
with time was observed for periods up to 1 sec. using repetitive pulses
and varying the sweep rate of the oscilloscope.

## Results and Discussion

A family of potential-time relaxation curves is shown in Figure 6A for $Fe(CN)_6^{4-} = Fe(CN)_6^{3-} = 0.1; 0.01; 0.001;$ Molar. The sweep rates are indicated in the captions. In all instances the voltage scale on the y axis was 1 mV. per graticule division.

It is known that for a given capacitor, the potential to which it may be charged is directly proportional to the change in charge density.

Thus q coulombs = C farads V volts. Hence for one charged capacitor discharging into another (the double layer), the initial charge = $q_o$.

$$q_o = C_1 V_1 = (C_{dl}^* + C_1) V_2 \qquad (25)$$

so that when $C_{dl}^* \gg C_1$ this becomes

$$q_o = C_{dl}^* V_2 \qquad (26)$$

where $C_{dl}^*$ = experimental double layer capacity.

On discharge, we have

$$\frac{dq}{q} = - \frac{dt}{C_{dl}^* \cdot R_a} \qquad (27)$$

Where $R_a$ is the electron transfer resistance.

$$\text{Integrating, } \ln q = \frac{-t}{C_{dl}^* \cdot R_a} + \text{const.} \qquad (28)$$

When t = o, q = $q_o$; then const. = $\ln q_o$

$$\text{so that } \ln \frac{q}{q_o} = \frac{-t}{C_{dl}^* \cdot R_a} \qquad (29)$$

$$\text{and } \frac{q}{q_o} = \exp. \left[ \frac{-t}{C_{dl}^* \cdot R_a} \right] \qquad (30)$$

$$\text{As } R_a = \frac{RT}{nF} \cdot \frac{1}{i_o} = \frac{RT}{n^2F^2 \, [c]} \cdot \frac{1}{k} \tag{31}$$

$$\text{for } i_o = knF \, [c] \tag{32}$$

where $[c]$ is the geometric mean of the concentrations of oxidized and reduced species, then equation (30) becomes:-

$$\frac{q}{q_o} = \exp. \left[ - \frac{k}{c_{dl}^*} \cdot \frac{n^2F^2}{RT} : [c] \cdot t \right] \tag{33}$$

and as $q = c_{dl}^* \cdot \eta$

and $q_o = c_{dl}^* \cdot \eta_{t=o}$

$$\text{then } \frac{\eta}{\eta_{t=o}} = \exp. \left[ \frac{-k}{c_{dl}^*} \cdot \frac{n^2F^2}{RT} \cdot [c] \cdot t \right] \tag{34}$$

and a plot of $\log \eta$ vs. $t$ has a slope of

$$\frac{-k}{c_{dl}^*} \quad \frac{n^2F^2}{2.303 \, RT} \cdot [c] \cdot \tag{35}$$

A full analysis of the problem with and without mass transport has been given by Delahay[24].

Plots of $\log \eta$ vs. $t$ are shown in Figure 7A. At short relaxation times a linear function is obtained. Deviation from linearity after about 10% of the potential decay has occurred is to be expected, as the surface concentration of the electroactive species is altered significantly from the initial state by the electrolysis. It is assumed that the initial surface concentration of the electroactive species at the electrode is the same as that in the bulk of the solution.

The kinetic rate constants derived from the analysis in Figure 7A are given in Table II. These results are compared with kinetic rate

constants obtained by other techniques. It may be seen that extremely good agreement is shown with results obtained in similar concentrations of reactants.

There is a distinct change in the apparent rate constant with concentration of the reactants and an explanation may be put forward.

It is possible that the surface concentration at the electrode is not the same as the $\smile$ the bulk of the solution. The high concentrations of chloride ions in $\smile$ $\ldots$lutions would be very strongly adsorbed and competing for sites on the electrode surface with the ferricyanide and ferrocyanide ions. Therefore as the concentrations of the ferricyanide and ferrocyanide increase in the solutions, the increase in the electrode surface coverages would not be as great as the bulk increase.

The range over which the kinetic rate constant may be obtained by this technique extends from $k=5 \times 10^{-5}$ cm. sec.$^{-1}$ to $k=1 \times 10^{3}$ using conservative values in the equation for the concentration and time of relaxation. Thus the pulse technique covers the range from irreversible reactions $(k < 10^{-4})$ to extremely fast reactions $(k > 1)$.

TABLE II (In all instances the supporting electrolyte was 1M KCl)

| | $k$ (cm. sec$^{-1}$) | $C$ oxidise' $= C$ reduced $= C$ (moles l$^{-1}$) |
|---|---|---|
| Randles & Somerton[25] (Faradaic impedance) | $9.0 \times 10^{-2}$ | $1 \times 10^{-3}$ |
| Jordan & Javick[26] (Rotating bucket) | $8.0 \times 10^{-2} \pm 1.0 \times 10^{-2}$ | $1 \times 10^{-3}$ |
| Agarwal[27] (Faradaic Rectification) | $6.6 \times 10^{-2}$ | $1 \times 10^{-3}$ |
| Jahn & Vielstich[28] (Rotating disc) | $5.0 \times 10^{-2}$ | $1 \times 10^{-2}$ |
| Stonehart | $8.1 \times 10^{-2}$ | $1 \times 10^{-3}$ |
| (This work) | $5.0 \times 10^{-2}$ | $1 \times 10^{-2}$ |
| | $4.14 \times 10^{-2}$ | $1 \times 10^{-1}$ |
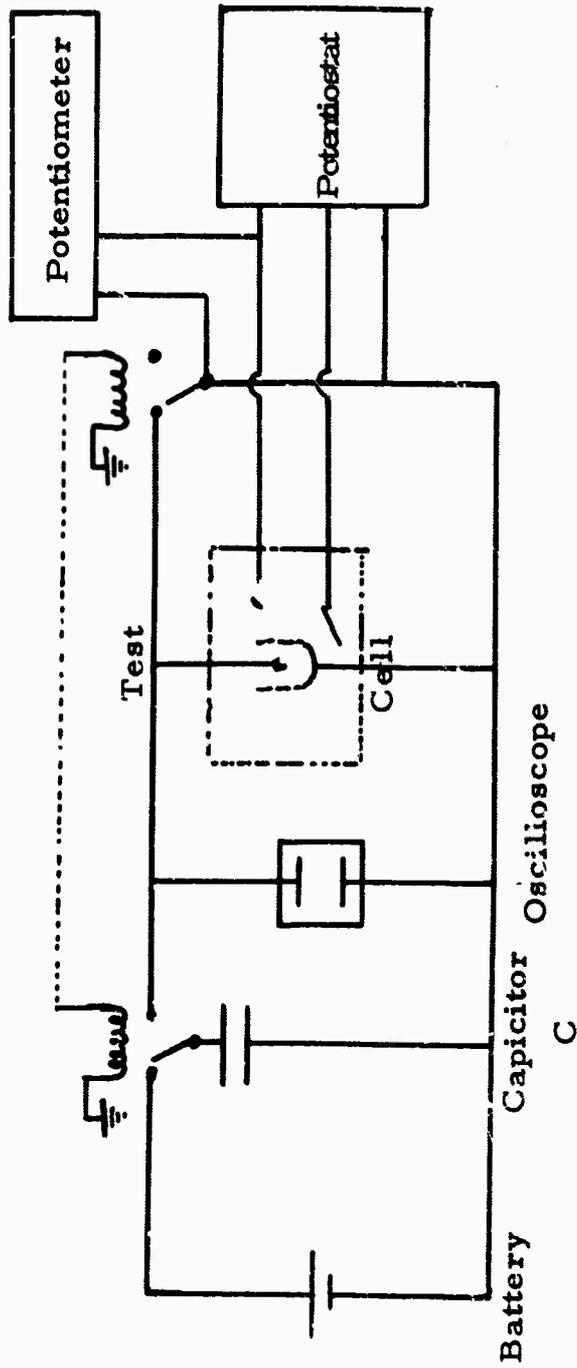
Figure 9A Pulsing "Coulostat"
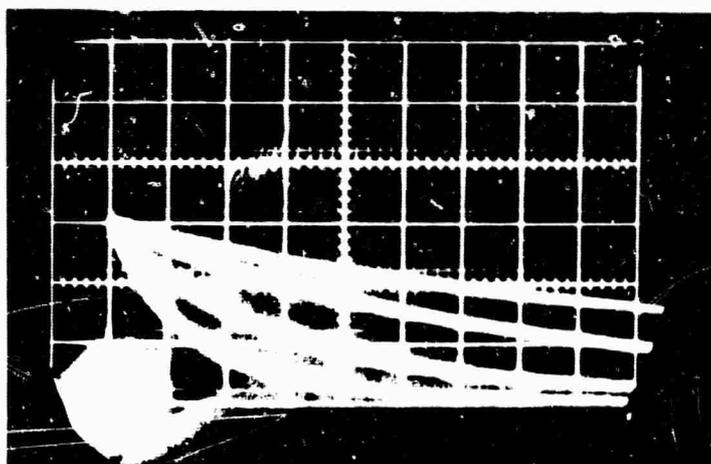
Figure 6A

    a.  $Fe(CN)_6^{3-} = Fe(CN)_6^{4-} = \cdot 1$ M. in 1 M. KCl.

    t = X axis = 1 μs; 2 μs; 5 μs; 10 μs per division

    b.  $Fe(CN)_6^{3-} = Fe(CN_6^{4-} = .01$M in 1 M. KCl.

    t = X axis = 10 μs; 20 μs; 50 μs; 1 ms per division

    c.  $Fe(CN)_6^{3-} = Fe(CN)_6^{4-} = .001$ M in 1 M. KCl.

    t = X axis = .1 ms; .2 ms; .5 ms; 1 ms per division
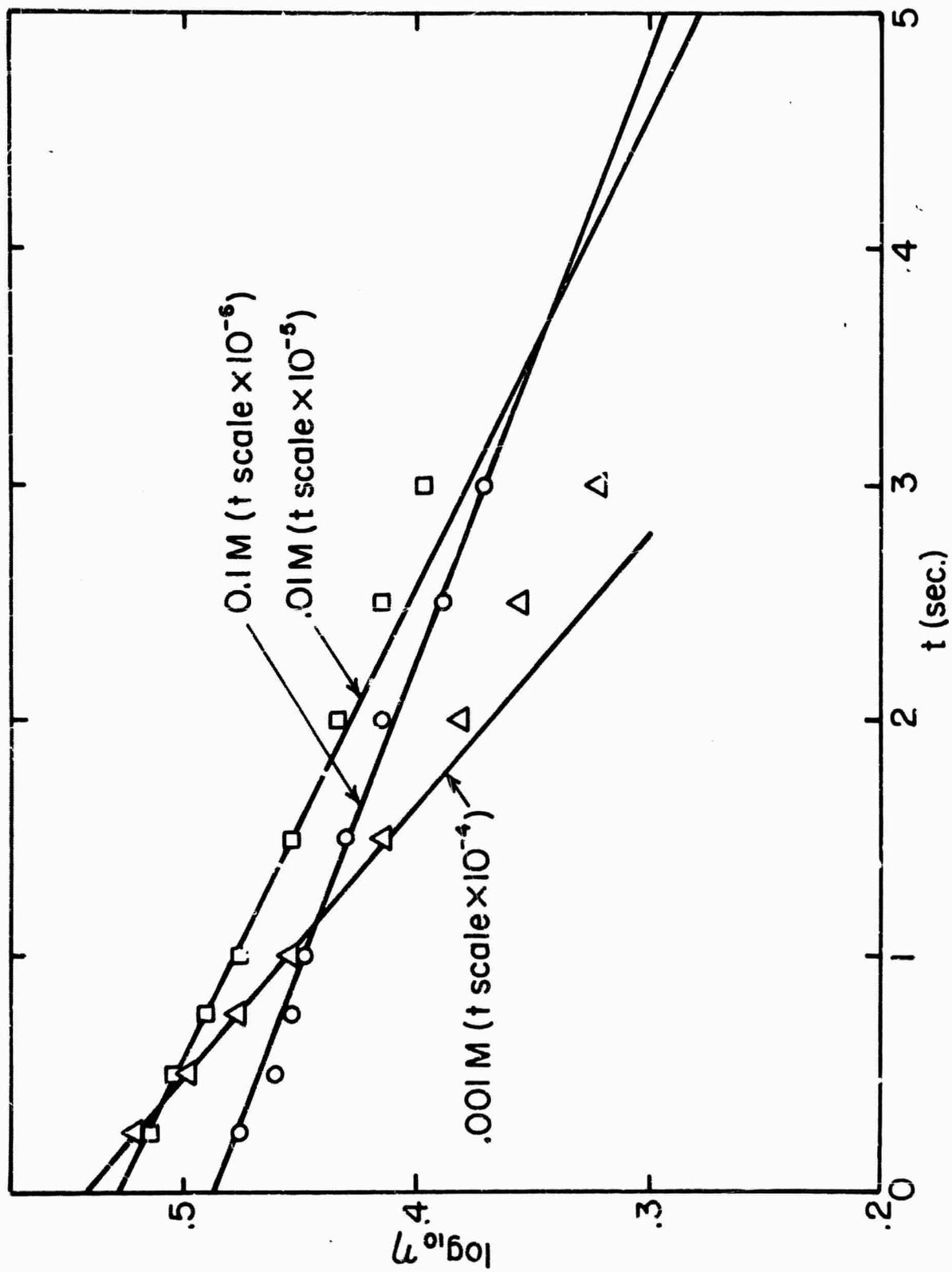
EQUIMOLAR FERRICYANIDE / FERROCYANIDE IN 1M KCl 29°C

Figure 7A

## Andrew's Titration for the Determination of Hydrazine

J. Amer. Chem. Soc. 1903.25.756

In strong hydrochloric acid solutions, the yellow crystals of iodine chloride are stable. Thus, iodine may be reduced to give an iodinium ion, $I^+$.

$$IO_3^- + 6H^+ + 4e^- \rightarrow I^+ + 3H_2O \qquad (36)$$

$$I^+ + Cl^- \rightarrow I\,Cl \text{ (yellow crystals)} \qquad (37)$$

With hydrazine

$$N_2H_5^+ \rightarrow N_2 + 5H^+ + 4e^- . \qquad (38)$$
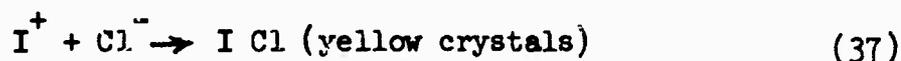
the overall reaction in strong acid is

$$IO_3^- + N_2H_5^+ + H^+ \rightarrow I^+ + N_2 + 3\,H_2O \qquad (39)$$

$$\text{Mol. wt. } IO_3^- = \text{Mol. wt. } N_2H_4$$

$$\text{and Equivalent wt.} = \frac{M.W}{4} .$$

The end point is detected on the point of complete removal of the iodine from solution. This is facilitated by having a few drops of an inert organic solvent in the solution and equilibrating the iodine so that a purple coloration in the organic solvent indicates excess iodine in solution.

### Technique

A clear glass stoppered 250 ml. bottle is used on the titration vessel. Into the bottle is placed 20 ml. conc. hydrochloric acid and 20 ml. water. 3 ml. of chloroform or carbon tetrachloride is then added. 20 ml. of the unknown hydrazine solution is added and the known potassium iodate solution run in from a burette.

An immediate brown coloration of iodine in the aqueous solution
and purple in the organic layer may be seen. The bottle is cautiously
shaken after each addition of iodate until only a faint purple color remains
in the organic layer. Dropwise addition of iodate is carried out until the
organic layer is colorless after shaking.

The intermediate reaction steps are as follows:

$$2IO_3^- + 3N_2H_5^+ \longrightarrow 2I^- + 3N_2 + 6H_2O + 3H^+ \tag{40}$$

$$2IO_3^- + 2I^- + 4H^+ \longrightarrow 2I_2 + 2H_2O + 4\bar{O} \tag{41}$$

$$2I_2 + 8H^+ + 4\bar{O} + 4e^- \longrightarrow 4I^+ + 4H_2O \tag{42}$$

$$N_2H_5^+ \longrightarrow N_2 + 5H^+ + 4e^- \tag{43}$$

giving overall;

$$4\ IO_3^- + 4N_2H_5^+ + 4H^+ \longrightarrow 4N_2 + 4I^+ + 12H_2O \tag{44}$$
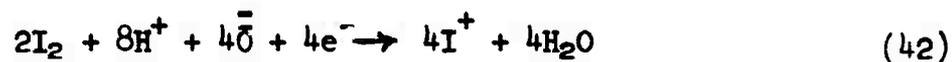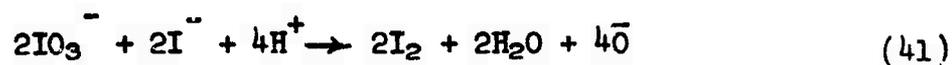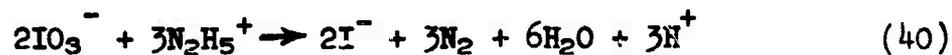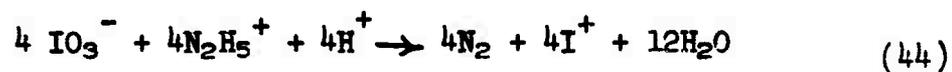
which is the previous equation.

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