THE PRESSURE DEPENDENCE OF HYDROGEN ADSORPTION ON A PLATINUM ELECTRODE

by

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I. INTRODUCTION

The hydrogen electrode is probably the most important and most widely used electrode in the field of electrochemistry. The hydrogen electrode has been used for nearly eighty years as the electrochemical standard by which all other electrode potentials are assigned.[1] The simplicity of its constituents makes this electrode ideal for study and analysis and its reliability makes it useful as a reference electrode when studying other electrochemical phenomena.

Catalysts, and platinum in particular, are extremely important in both the commercial and scientific fields. Nearly all hydrocarbon fuel used at present has been treated with platinum or some other cracking catalyst to break down long chain hydrocarbons to make them more easily combustible The use of platinum and other catalytic agents in fuel cell technology will insure their importance in the future as well.

Despite the fact that nearly all of platinum's catalytic properties are dependent on adsorption of reactants and that most reactions that platinum catalyzes involve hydrogen, the mechanics of the adsorption of hydrogen onto platinum, its configuration on the metal surface, and how it is bound there are at best only partially understood. Even though the hydrogen electrode has been studied for over sixty years, little is known concerning the relative importance of the various characteristics of the solution, the reactants, and the electrode. Bowden[2], in 1920, was the first to propose that hydrogen was adsorbed on the surface of a platinum electrode. Since then much work has been done attempting to relate the catalytic properties of platinum to its adsorption abilities. Some work has shown that the "d" character of the hybrid orbitals of atoms in the metal lattice are related to its catalytic activity in a qualitative way but, as far as a quantitative analysis of this behavior is concerned, a great deal of work remains to be done.

The present investigation concerns itself with the study of the pressure dependence of hydrogen adsorption on a platinum electrode in acid media. The specific intent of this work is to find whether additional hydrogen adsorbs onto a platinum electrode when the system pressure is increased. Through this means it is possible to prove or disprove the assumption usually made that hydrogen forms a monolayer on a platinum electrode at one atmosphere pressure. Secondary aspects of this study are the effects of diffusion of hydrogen atoms into the electrode bulk, and the desorption and diffusion of hydrogen molecules into the solution layer surrounding the electrode.

II. LITERATURE SURVEY

The electrochemical reaction of hydrogen deposition on platinum electrodes has been extensively studied for a number of years. The area of most intensive interest has centered on the characterization of the surface of the platinum electrode.

The exact mechanism of the hydrogen discharge and dissolution, or evolution, of molecular hydrogen is still in question. The possible mechanisms are the following:

I.	$H^+ + e^- = H(ads)$	Volmer Reaction
II.	$H^+ + H(ads) + e^- = H_2$	Heyrovsky Reaction
III.	$H(ads) + H(ads) = H_2$	Tafel Reaction

The first two reactions are controlled by the kinetics of charge transfer while the last one is controlled by the kinetics of surface diffusion.[3,4] Under other circumstances the mechanisms might be determined by consideration of stoichiometric numbers from experimental data but, in this case, the proper combination of the above reactions give three possible overall mechanisms.[3]

The kinetics of hydrogen adsorption on the surface of the platinum can be described using either the Langmuir or the Temkin isotherm equations[3]:

Langmuir isotherm

$$\frac{\theta}{1-\theta} = P \exp(-\Delta G_0/RT)$$

Temkin isotherm

$$\theta = \frac{1}{s} \ln P - (\Delta G_0 / sRT) + 0.5$$

θ = fractional coverage by atomic H

P = the pressure of H_2

ΔG_0 = the standard free energy of adsorption

R = gas constant

T = the temperature of adsorbed gas

s = constant depending on linear variation of the heat of adsorption on coverage

The Langmuir isotherm was found to work well below 20°C but, at higher temperatures, corrections were made to account for surface heterogeneity and adsorbate atom interaction. This modified Langmuir equation is known as the Frumkin equation. The Temkin isotherm works fairly well in the range of coverage of 0.2-0.8 but breaks down outside these limits.

The above equations have been used to develop equations for the equilibrium exchange current and the forward and reverse reaction velocities.[3]

The three most common means of studying the surface characteristics of an electrode are the galvanostatic, the A.C. impedance, and the potential scan method. The galvanostatic, or method of charging curves, was one of the earliest methods used and consists of passing a constant current between two electrodes and recording the potential variation produced.[5,6,7,8] The lower portion of the curve (Figure 1) corresponds to the hydrogen region where the hydrogen ion is discharged and adsorbed on the surface of the platinum. The curve begins to rise steeply at the beginning of the double layer region where the current is used almost exclusively for the charging of the electrode's double layer capacitance. The upper section of the curve is the oxygen adsorption region where the surface of the electrode forms an oxygen film layer.

This method is very sensitive to impurity and reactant concentrations in the cell and has been used extensively in the study of organic reactions on different types of electrodes.[7,9] Variations on this method include measurements in alkaline solutions, giving only qualitative results[8], and use of galvanostatic pulse techniques.[18]

Impedance measurements are made by equilibrating an electrode at a given potential and superimposing a small A.C. signal.[5,6,8] Capacity measurements are usually made using an A.C. impedance bridge which will give both capacity and phase data. With this one can distinguish double layer capacitive current and hydrogen evolution current from their phase differences. To give more complete information on the region of study the capacity curves have sometimes been coupled with a slow potential scan. Figure 2 is a potential scan-impedance curve of the hydrogen region.[5] The peaks shown correspond to the adsorption maxima of hydrogen on platinum. The shoulder on the largest peak has been attributed to a possible third adsorption site.[11] This method, like the galvanostatic, is very sensitive to the concentration of impurities or reactants being studied in the cell.[12,13,14,15]

The linear potential scan method, which has been used in this study, will be considered in greater detail than those described above. Figure 3 is a potentiostatic curve over the region generally studied using the linear potential scan method. The voltage range is from 0V to 1.6V versus the normal hydrogen electrode and covers the phenomena from hydrogen evolution to oxygen evolution. The most cathodic section of the curve is known as the hydrogen region; the second section of the curve is the double layer region, and the third, the oxygen adsorption and evolution region.

The hydrogen region extends from 0V to approximately 0.4V. Hydrogen coverage on the electrode is potential dependent and is responsible for the two peaks shown. The maxima correspond to differences in the heat of adsorption of hydrogen on platinum. Hydrogen adsorption is reversible on platinum as is seen by the mirroring effect of the cathodic and anodic wings of the curve.[16] The source of the reversibility is that any current used to discharge and adsorb hydrogen ions is recovered at the same potential at which it was given up when the atomic hydrogen loses an electron and is returned to the solution.[4,5] The only difference between the cathodic and anodic charges should come from molecular hydrogen dissolving into the solution or hydrogen atoms diffusing into the metal lattice.

The double layer region of the curve is the potential region in which there is virtually no adsorption or desorption going on and where all the current goes to charge the double layer of the electrode.

The oxygen region of the electrode is the potential interval in which an oxygen film is formed on the electrode and eventually, at sufficiently high potentials, oxygen evolution begins. The oxygen adsorption-desorption reaction is nonreversible as can be seen from the asymmetry of the curve. During the anodic sweep oxygen will adsorb at an approximately constant rate up to the evolution potential, however, during the cathodic sweep, no oxygen desorbs until a moderately cathodic potential is obtained where the oxygen desorbs in one peak.

It can be shown[5] that the capacitive or reversible sections of the potentiostatic curve corresponds to the derivative of the equivalent portions of the galvanostatic curve. Through this means the potential sweep curve is capable of much higher resolution of the important maxima than the galvanostatic curve.

Shown in figure 4 is the region that was considered in this study.[5] The point chosen for the termination of hydrogen adsorption and the beginning of hydrogen evolution is an arbitrarily chosen point. The particular method used here is said to give fairly reproducible results at sweep rates up to 800V/sec.[13] Various means have been employed to choose a potential at which the electrode is said to have full hydrogen coverage and nearly every method has yielded a different result. Depending on who is cited, the values range from -0.01V to 0V versus the NHE.[5,8,13] The importance of this particular point stems from the idea that one can calculate the surface area of the electrode from the amount of charge used to adsorb a full layer of hydrogen. In order to do a calculation of this form it is necessary to know the points of zero and full coverage as well as the ratio of surface platinum atoms to hydrogen atoms. Numbers usually obtained for full monolayer coverage range around 210 microcoulombs/square centimeter.

As previously mentioned, the A.C. impedance curves show a shoulder on the cathodic side of the largest peak in the hydrogen region both of which drop to very nearly zero at about 0.01V. It might be reasonable to assume that this would be where adsorption would come to a halt. Difficulty would still remain in deciding what proportion of the current prior to 0.01V would be due to hydrogen evolution and it is likely that some other measurement would be needed to determine this value. The point of zero hydrogen coverage is usually assumed to be the point of inflection between the double layer region and the first rise in the adsorption curve.[5]

The correction for double layer charging current is usually determined in the double layer region and then extended over the entire potential range studied.[5,6,8] The value given for the coulombs used in double layer charging varies over a wide range but the generally accepted values are in the range of 2% of the total current uptake and are therefore considered insignificant.[5,6,8]

In the curve of Figure 4 the most commonly observed hydrogen adsorption peaks are shown. The actual number of peaks and the significance of the various maxima in this region are still a matter of controversy. The generally accepted justification for the peaks being at different potentials is that the heat of adsorption of hydrogen is different for the two types of adsorption. The exact mechanism involved for the hydrogen adsorption under each of these peaks is in question. One of the earlier mechanisms proposed was that by Euken and Weblus[17,18] who asserted that the weakly adsorbed hydrogen was atomic hydrogen adsorbed on Pt-O while the strongly bound hydrogen was adsorbed on metallic platinum.

More recently three possible explanations have been proposed for the different maxima: a change in the work function with increasing adsorption, adsorbed atom interaction (weakest), and heterogeneous character of the electrode surface.[3] Substantiation for the first two proposals comes from data showing that the first 40% of the adsorbed hydrogen is strongly bound in both solution and the gas phase.[6,8] Gas phase work has also shown that, after a monolayer coverage has been established, a high vacuum can remove 60% of the adsorbed hydrogen but not the remaining 40%.[6] Other work has shown that the first 40% of the hydrogen adsorbed is the negative end of a dipole[8] and has the effect of increasing the work function of the platinum. Field ionization work[6] has shown that, after an initial rise, the work function of the metal will decrease. Data indicating that the last 60% of the hydrogen adsorbed is the positive end of a dipole has also been reported.[6,8] Infrared spectra using hydrogen as well as mixtures of hydrogen and deuterium indicate that the hydrogen is atomically adsorbed on the platinum surface.[8,19]

Breiter[10] has found that hydrogen adsorption can be described by two overlapping Frumkin isotherms. However, this analysis does little to resolve the question since this result can describe either similarly bonded hydrogen on two different sites or differently bonded atoms on similar sites.

More recently work by Will[6] has indicated that hydrogen binding on different crystal planes may be responsible for the different peaks. Will's work used platinum single crystal faces exposed to the solution for each of the low index planes: (100), (111), (110). The result of this experiment showed that there were definite differences in the relative peak heights depending on the different face exposed (Figure 5). Data has also been reported indicating that the free energy of adsorption is relatively constant within a given peak but varies from one maximum to the next.[19,20] This type of discontinuous behavior would be expected for heterogeneous adsorption sites but not homogeneous absorbate atom interaction or for changes in the platinum-hydrogen interaction.

Arguments against the findings of Will have been made on the grounds that he mechanically flattened the surface of his single crystals thereby causing faceting and exposure of different planes on the atomic level.[5] Although this argument carries some merit, it would seem logcial to assume that statistically more area of the nominally exposed face would be present than whatever others were generated by polishing.

Will's work also indicated that there might be a maximum in the current-potential curve somewhere between the two maxima seen in most other curves

(Figure 5).[6] Peaks at potentials different than those shown in Figure 4 have been observed on platinized platinum and in different solutions[11,21,22,23] but most have been disputed as being due to adsorbed anions or impurities.[5,6,22,24]

Production of valid hydrogen adsorption curves has been found to depend on the following: sufficient time for equilibration of the electrode, avoidance of diffusion of molecular hydrogen or contaminants to the electrode surface, and maintenance of a clean active surface.[5]

Large variations in what is considered to be an acceptable sweep rate to satisfy the first of the above conditions have been found. Rates ranging from 30mv/sec up to 800v/sec have been used in various experiments.[5,6,8] Justification for slow sweep rates comes from work indicating that the adsorption of hydrogen is either diffusion controlled or controlled by the slow equilibration of $H_2 \rightleftarrows 2H$.[3,6,8,11] Those who favor high sweep rates feel that their results are sufficiently reproducible, up to 800V/sec, to validate their work.[5,13]

Adsorption characteristics of impurities and surface active ions onto platinum electrodes have received a great deal of attention. It has generally been found that the order of the activity of anion adsorbability follows the sequence: $OH^- < ClO_4^- < SO_4^{=} < Cl^- < Br^- < I^-$. The last two members of this group, the bromide and iodide ions, have been found to have effects similar to such typical catalytic poisons as mercury and the cyanide ion.[8] There has been some dispute over the strength of the ability of the chloride ion to strongly adsorb[25] but, under specific conditions (H_2SO_4, 0.5 molar), its presence can cause the appearance of a new peak in the hydrogen region.[22] This work (22) also finds an added maximum when using 1 molar sulfuric acid indicating that high concentrations of $SO_4^=$ can behave much like the chloride ion in its adsorption activity. It is generally accepted that the perchlorate ion has a very low surface activity and is a fairly reliable electrolyte when doing adsorption work.[5,7]

Similarities have been drawn between the effects of anion adsorption and an increase in the temperature of the electrolyte. The correlation made was that, with anion adsorption, a more cathodic potential was necessary to attain the same coverage as is the case with increased temperature. More detailed analysis of the effects of anions has shown that different anions affect different adsorption sites.[16,24] Some work has indicated that the anions poison or adsorb on the sites that are usually occupied by the strongly bound hydrogen while leaving unaffected the weakly binding sites.[6] Other work implies that some anions adsorb onto sites that are not active with hydrogen since their adsorption and desorption potentials are displaced from those of hydrogen.[22,24] This analysis is open to question since it cannot be assumed that an adsorbed ion on any given site will be adsorbed with the same energy as a hydrogen atom on that site.

Studies on solution purity with respect to organic contaminants has been relatively extensive. Most indications are that, given proper cleaning of equipment and properly distilled water, an electrode will remain comparatively free of contaminants for up to 100 seconds in an unstirred solution.[13,24] As would be expected, this time is considerably reduced in a stirred solution. The most common procedure for obtaining a purer solution than ordinarily possible through proper cleaning techniques was to pulse a larger surface area electrode to a highly anodic potential over a period of hours.[13] Accepted procedure for cleaning an electrode prior to a curve scan is the following: the electrode is pulsed to an anodic potential (1.8V) for a few seconds, the potential is returned to a point somewhere in the oxygen region (approximately 1.4V) to allow the evolved oxygen in the solution to disperse, the potential is then dropped to the potential at which the scan will start (approximately 0.4V).[15,13,26] This procedure gives a clean reduced platinum surface.

Other potential variables that need to be taken into account when working with the hydrogen-platinum system are: temperature effects, electrode surface roughening, and possible absorption of film layers into the bulk of the electrode.

The variations in coverage caused by changing temperature have been well documented.[5,13,20] Bold and Breiter[27] have shown that, for a given potential range, the coverage is decreased as the temperature is increased. It has been shown that the effect of a temperature increase is to shift the potential curves in the cathodic direction and that this shift can be related to the overall heat of adsorption through the Nernst equation and the Clapeyron-Clausius equation.[5] Breiter[20] and others[23] have interpreted data from temperatures exceeding 70° C as indicating that hydrides are formed on the surface of the platinum electrode in this range of temperatures.

The effects of electrode surface roughening have been found in a number of experiments. The work done by Will[6] gives strong indication that, during use, the surface of the electrode will rearrange on the atomic scale to expose different faces. Other work has shown that there is a general increase in total electrode surface area over the course of an experiment.[5,6,13,26]

Numerous reasons for the increase and methods for its prevention have been suggested. Most work has indicated that highly anodic polarization of the electrode causes roughening and, in some cases, platinum has been reported to have been carried into the solution.[5,6,11,13,26] High sweep rates have also been related to extensive surface roughening.[5,13,26] Proposals for preventing this roughening include the obvious remedy of reducing the time spent under anodic polarization and reducing the scan rate. Alternate remedies suggested have been immediate reduction following oxidation[26], bubbling of nitrogen gas through the solution[26], and a variety of others.[5,6,11,13]

Biegler and coworkers[11] have found effects other than roughening when the surface has been severely oxidized. The interpretation proposed was that oxygen had diffused or had otherwise gotten into the bulk of the electrode. Work in other groups has indicated that hydrogen might also be able to absorb into the bulk platinum as well.[5,13,16] Substantiation for hydrogen absorption to any appreciable degree has been very sparse while the question of the form of oxygen on the platinum surface still remains open to question.[5]

The results of many of the above experiments have been checked by independent means with varying degrees of success. Gas phase work has been done, as already mentioned, to try to determine the binding states of hydrogen on platinum.[5,6,28] Infrared and field ionization work have also been done with this same question in mind.[5,6] Extensive work has been done using other metals for electrode material giving useful insight into a number of questions that have been raised.[5,8,28] Correlation of surface area measurements using krypton gas at low temperatures has given fair agreement with values obtained electrolytically.[8]

In summary one can see that a great deal of work has been done involving the surface of the platinum-hydrogen electrode. A substantial amount of time has been spent studying the relationship between the amount of hydrogen adsorbed and the surface area of the electrode in question.[3,4,5,6] In all of these studies the assumption has been made that there is a monolayer coverage achieved on the electrode at some potential near 0v versus NHE. The assumption has also been made that there is no pressure dependence of this point of full coverage. The intent of this study is to test the validity of this last assumption.

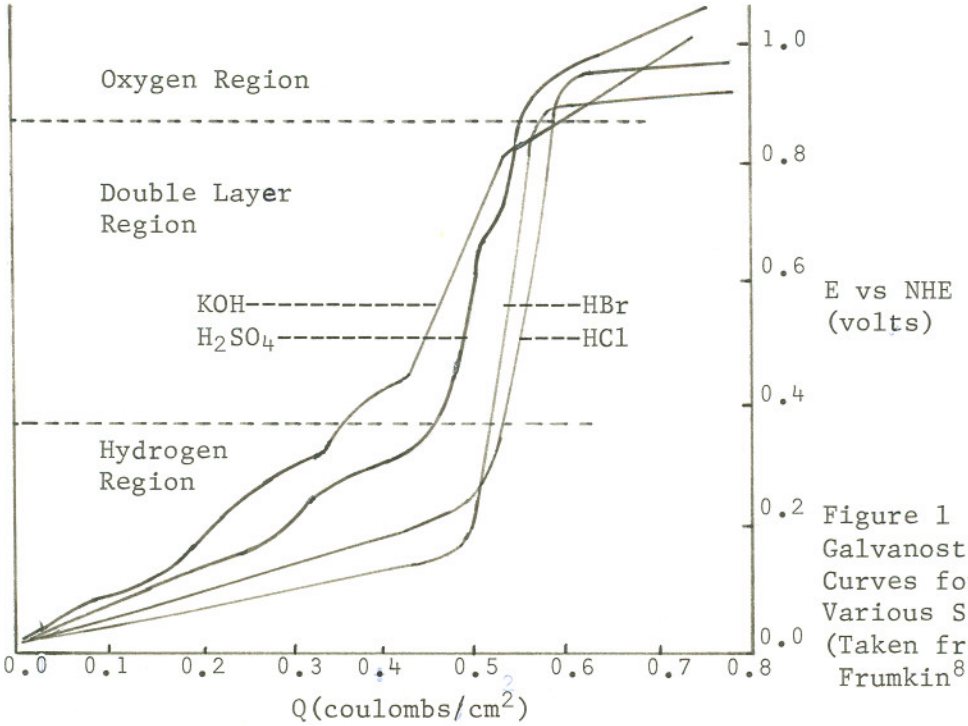


Figure 1
Galvanostatic
Curves for
Various Solutions
(Taken from
Frumkin[8])

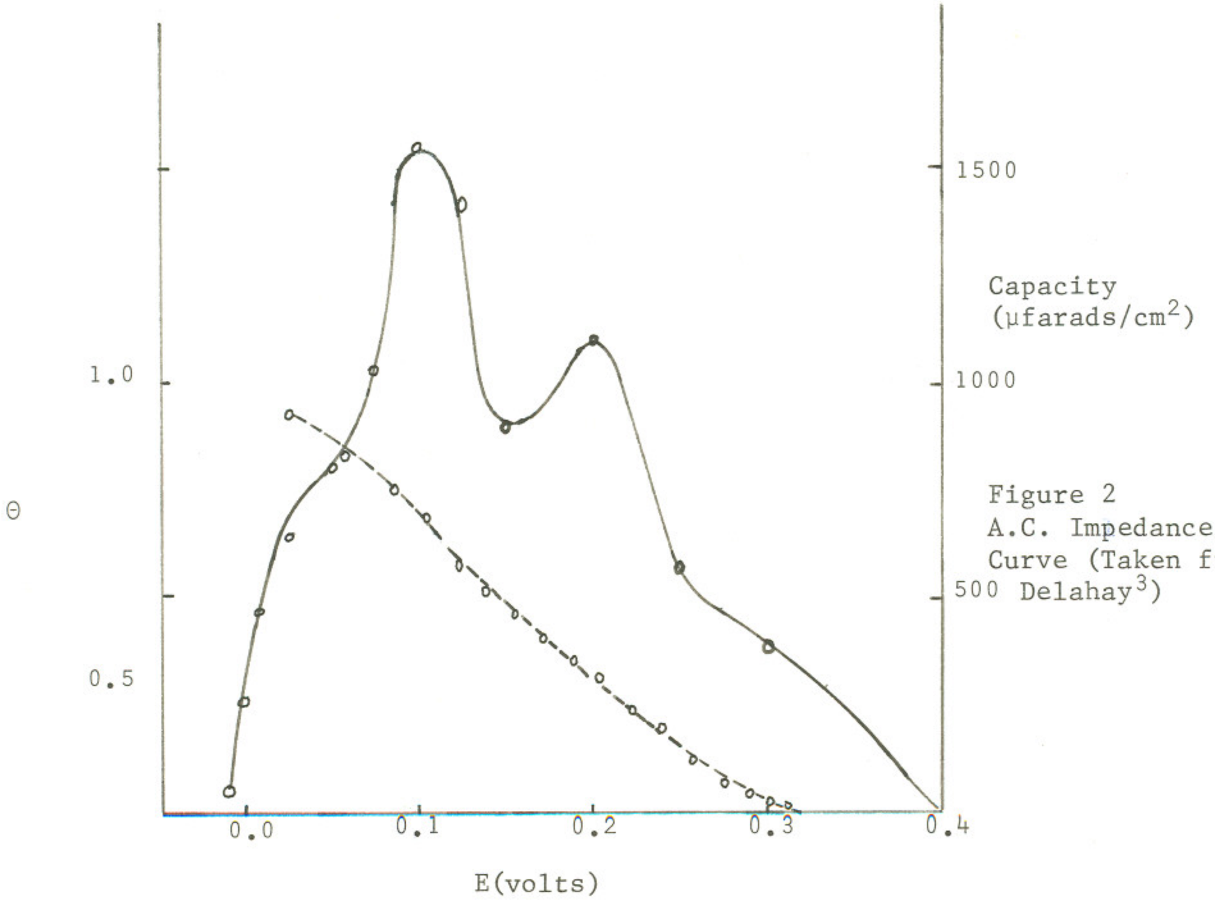
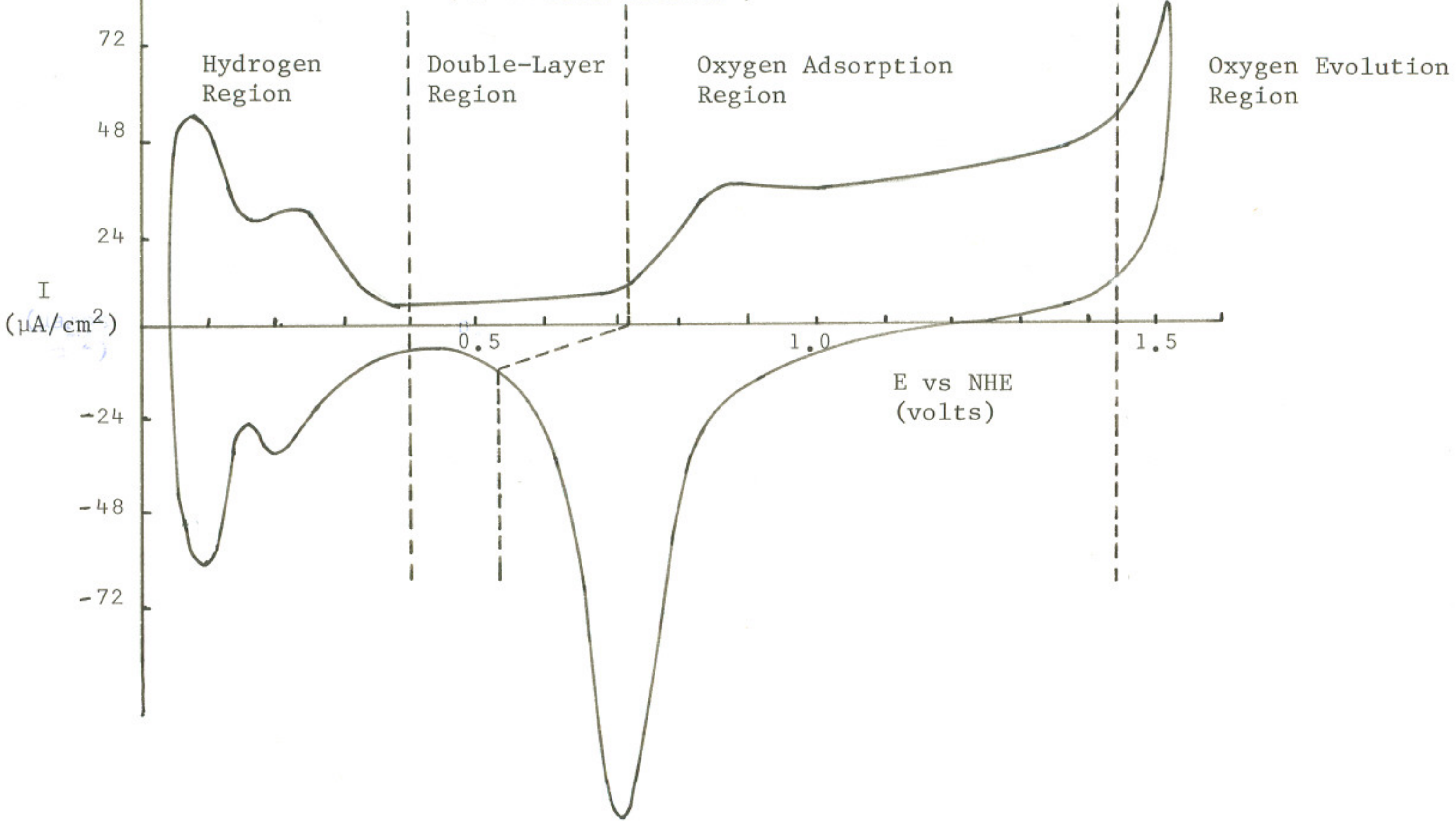


Figure 2
A.C. Impedance
Curve (Taken from
Delahay[3])

Figure 3
Current-Potential Curve For a Smooth Platinum Electrode (Taken from Breiter[7])



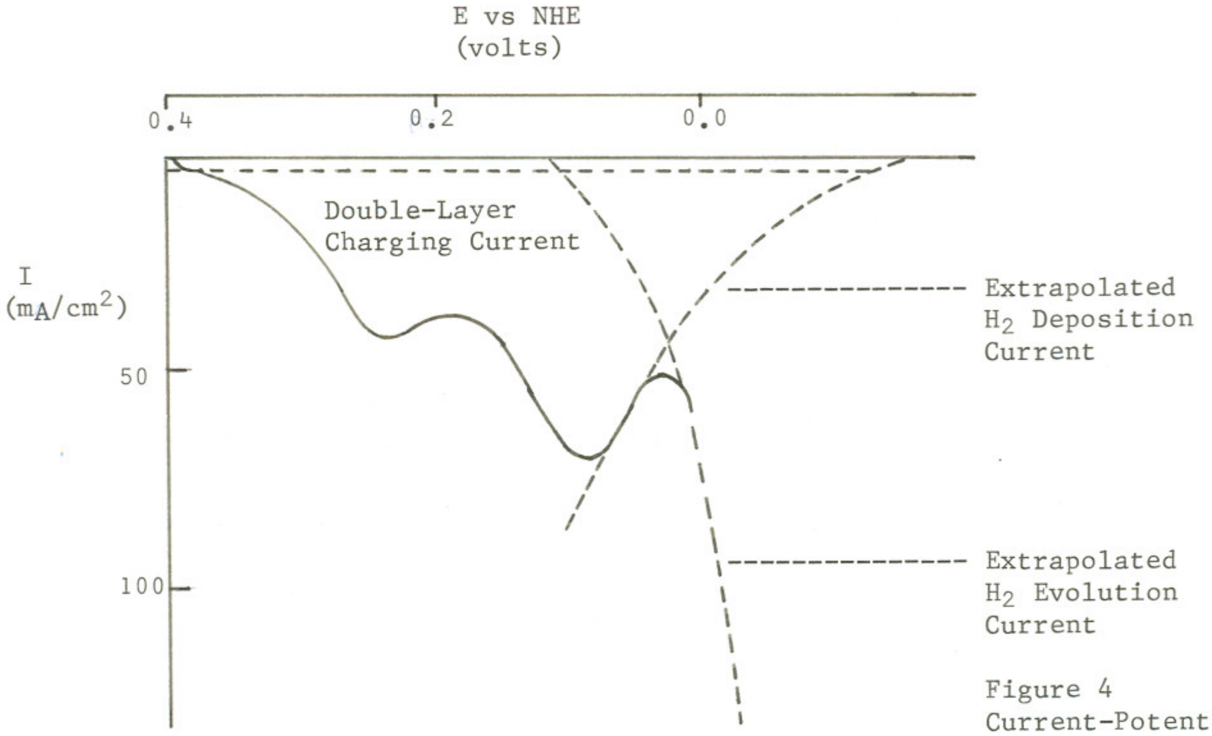


Figure 4
Current-Potential
Curve (From Gilman[8])

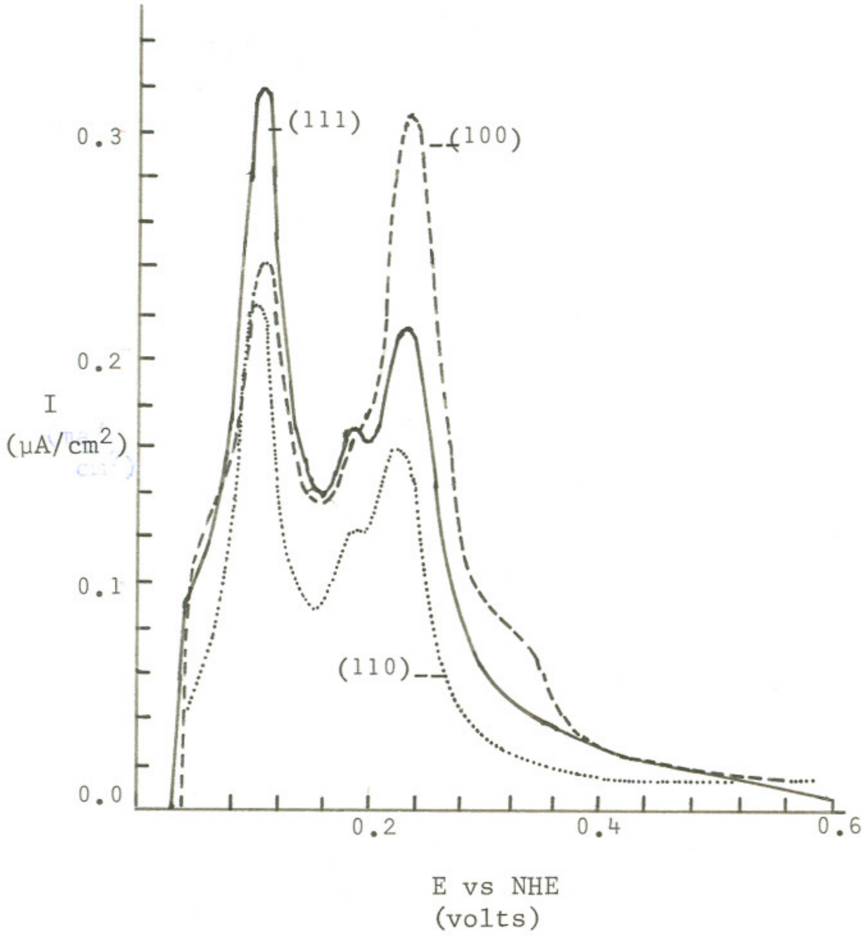


Figure 5
Current-Potential
Curves on Different
Electrode Crystal
Planes
(Taken from Will[6])

III. EXPERIMENTAL

The experimental set-up was as shown in Figure 6. The helium used was originally 99.99% purity from Lif-O-Corporation and, later, helium purified by being passed over molecular sieve at liquid nitrogen temperature. The gas scrubber consisted of a fritted disc immersed in a suspension of platinum black in one molar perchloric acid. The platinum black was generated by reduction from chloroplatinic acid using sodium borohydride. The perchloric acid was from Mallinckrodt, 70% AR grade, with impurities of approximately 0.0035%: chloride, sulfate, and nitrogen compounds 0.001% each, with an additional 0.0005% silicon and phosphorus impurities.

The perchloric acid in the scrubber was of the same concentration as that used in the electrode cell. The reason for this procedure was that it was felt that anything that might adsorb onto the electrode would be taken out of the gas train by the high surface area platinum black. Another benefit was that the helium would be saturated with perchloric acid and water vapor before it got to the electrode cell and therefore could not evaporate solution from the electrode cell. The pressure cell and electrodes were as shown in Figures 7 and 8. The pressure gauge was from Marsh Instruments Company, type 220-C, 0-150 pounds with 1 pound subdivisions. The back pressure regulator was from Apco, 1103 series, and the flow meter was in-house made.

For measurements at reduced pressures, the back pressure regulator was replaced with a cold trap and Welch vacuum pump. The pressure readings were taken with a mercury manometer at a point between the cell chamber and cold trap.

In order to maintain a steady working pressure, the needle valves controlling the gas input and the pumping rate were manipulated. The input valve was first set at a very slow flow rate after which the valve to the vacuum pump was adjusted to give a steady pressure reading over a period of minutes This time was sufficient to allow all the necessary measurements to be made. The above described system allowed data to be taken at pressures ranging from twenty-six millimeters of mercury up to nine atmospheres. The accuracy of the high pressure readings was in the range of a half pound while those at reduced pressures were known to within three millimeters of mercury.

The electrical system consisted of a potentiostat, designed and built by Prof. D.K. Roe, a recorder made by Electronic Associates Incorporated, type 1131 Variplotter, and a digital voltmeter, Fairchild model 7050.

The Fairchild voltmeter provided cell voltages accurate to within five millivolts while the potentiostat could be relied upon to give current and coulomb measurements accurately to within three tenths of a microamp and two tenths of a microcoulomb, respectively.

The cell chamber (Figure 7) was designed to allow studies at both elevated and reduced pressures; the most notable feature is an "O" ring which can form a seal with pressure from either direction.

In order to minimize the voltage drop between the indicator and reference electrode (R.E.) the fitting for the reference electrode was angled to allow the end of the two electrodes to be positioned as closely together as possible.

A hydrogen electrode was employed as a reference for potential measurement and control. Hydrogen gas required for this electrode was generated with a small constant current applied between two platinum wires inside the small cell formed by the reference electrode tube. A battery was chosen as the current source in order to isolate the reference electrode from any perturbations that might be caused by the rest of the electrical system. It was found that approximately 0.18 milliamp was sufficient current to maintain a steady potential without excessive bubbling of evolved hydrogen.

Other features of the R.E. are seen in Figure 8. The Vycor plug in the tip allowed electrical contact with the main cell while preventing any cross contamination between the R.E. and the cell. The platinum wires inside the electrode are isolated from each other at various points by being clad in glass. This action was taken to prevent any side reactions from taking place between the gaseous hydrogen and oxygen at the platinum-solution interface. In order to remove the hydrogen and oxygen generated inside the R.E. a vent was put in the glass tube above solution level. This also allowed pressurization of the reference electrode whenever the cell pressure was changed.

The indicator electrode (I.E.) was built in two parts. The upper section consisted of a tungsten rod sealed into the top and extending down the length of a glass tube. At the lower end of the tungsten rod was welded a small pin clip. The lower section consisted of a soft glass tube of a diameter that would fit snugly inside the end of the upper part of the electrode. Inside this tube was a copper wire which fit the pin clip at the end of the tungsten lead. The copper wire was soldered to a platinum wire sealed into the lower end of the tube. The intent of the two part assembly was that the lower section of the electrode could be replaced without remaking an entirely new electrode.

When making the lower section of the I.E., enough platinum wire was left exposed outside the seal so that it could be melted into a bead approximately 0.14 centimeter in diameter. When the wire was melted to form the electrode the bead was cooled very slowly to prevent bubble craters or other irregularities from forming in its surface. It was also necessary to partially seal this bead into the end of the glass tube to prevent the nonuniform surface of the wire from coming into contact with the cell solution.

The other electrodes in the cell were a pair of counter electrodes. Their design was fairly standard with platinum gauze exposing to the solution a large active surface area, relative to the indicator electrode. The only notable feature of the counter electrode's construction was that the glass tubes were vented to the inside of the cell above solution level. This was done when it was discovered that small amounts of solution, after being forced into the glass tubing at high pressure, returned to the cell solution at lower pressures causing extensive contamination.

After it was found that the solution was contaminating itself by being splashed onto the cap of the pressure casing and then dropping back into the

the cell, a teflon shield was suspended above the solution. The teflon was cleaned with the rest of the assembly and was otherwise considered inert. It was also necessary to put bulges in all the electrodes just below their fittings to prevent them from being blown out of the cell when it was being used at high pressures.

Before the cell was assembled the glassware and teflon were boiled in a 3:7 solution of nitric-perchloric acid for at least one half hour to remove any organic residue on the glass or the electrodes. While this was being done it was necessary to take great care with the indicator electrode since the platinum bead was very soft and easily scratched. Everything was then rinsed with water which had been triply distilled from a quartz still.

The cell was then assembled and filled to the appropriate level with perchloric acid solution. After the lower section of the cell had been tightened onto the cap, helium was bubbled through the solution. A power supply, at a potential of 1.8V, was connected to the two counter electrodes and the solution was pre-electrolyzed for twelve to twenty-four hours. This procedure oxidized most of the lingering organic contaminants and allowed the helium to sweep the reaction products out of the cell. Following preelectrolysis, the solution was allowed to stand for three to four hours to enable any peroxides formed by electrolysis to decompose on the platinum surfaces in the cell. This time also allowed the helium to clear the cell of any reaction products of the electrolysis.

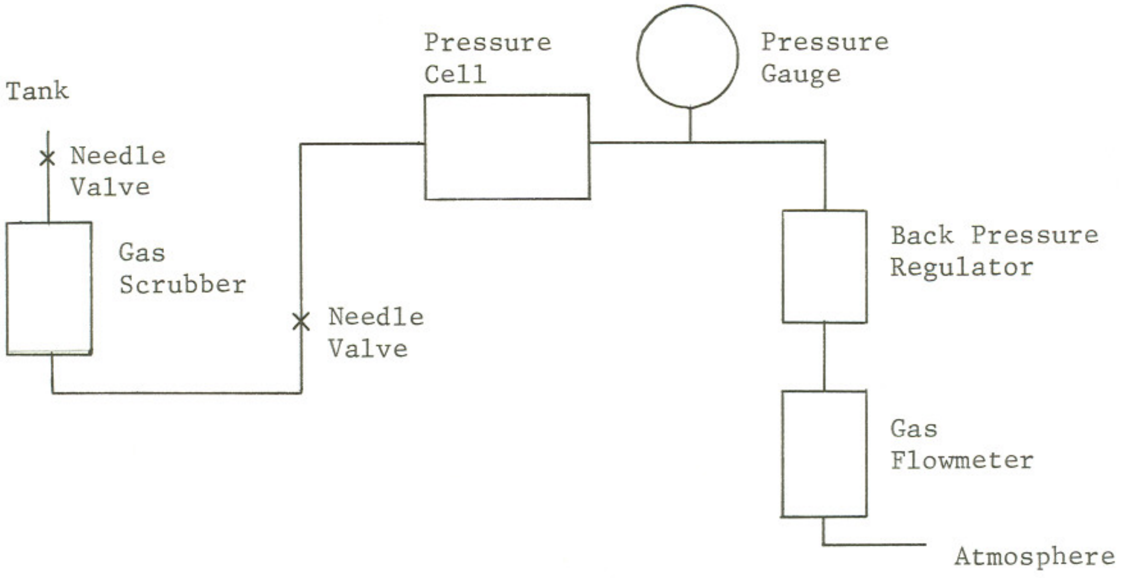
Even though the solution had been cleared of most organics, contamination was still visible in the data curves unless the indicator electrode was prepared before each voltage scan. The precleaning procedure consisted of pulsing the I.E. to approximately 1.8 volts a number of times. An alternate procedure was to hold the I.E. potential a few millivolts cathodic of oxygen evolution and then , very rapidly return it to the voltage at which the scan was to begin. Both procedures seemed to work equally well.

Since the adsorption of organic contaminants is diffusion controlled, the time allowed between the cleaning operation and the potential scan was kept to a minimum. When taking a data curve the best procedure was to start the potential scan simultaneously with the recorder scan. The recorder was run in the time mode and plotted both the current curve and its integral,the coulomb curve. Since the voltage was being scanned at a constant rate with respect to time, it was very simple to convert both the current and coulomb curve back to the potential axis giving the usual current-potential curves.

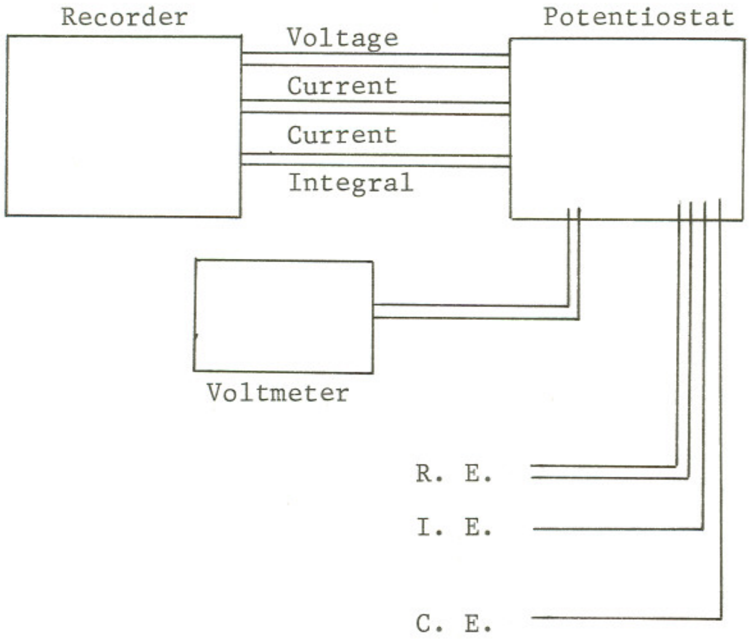
By running the recorder in the time mode the direction of scan could be reversed at any point, in most cases just short of drastic hydrogen evolution, and returned to its starting potential without having the curve fold back on itself.

The procedure for taking data for the hydrogen desorption and contaminant reduction current was very nearly identical to that for the normal data curves. Instead of running a complete curve, the scan was stopped at points along the curve and the current was allowed to decay with time on the recorder trace. By doing this at a number of points it was then possible to obtain a curve that could be related to hydrogen desorption and contaminant reduction current.

After sufficient data had been taken to justify a statistical analysis, the indicator electrodes were removed from the cell and photographed using a Leitz photomicrograph. Pictures were taken from four sides and the bottom of the electrode. From the photographs it was then possible to calculate the geometric surface area of each of the indicator electrodes.



Gas Train



Electrical System

Figure 6
Block Diagram

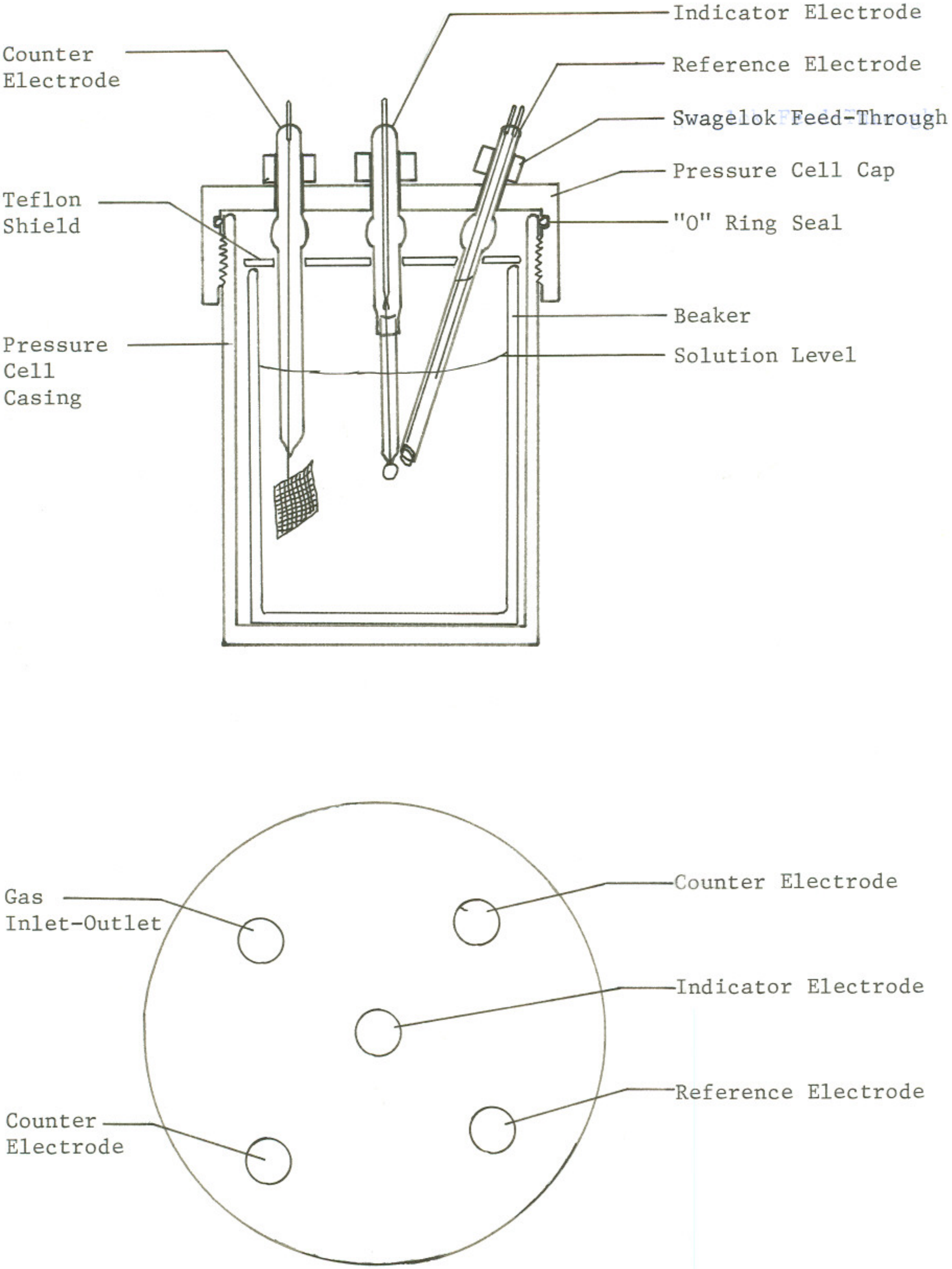


Figure 7
Pressure Cell Diagram

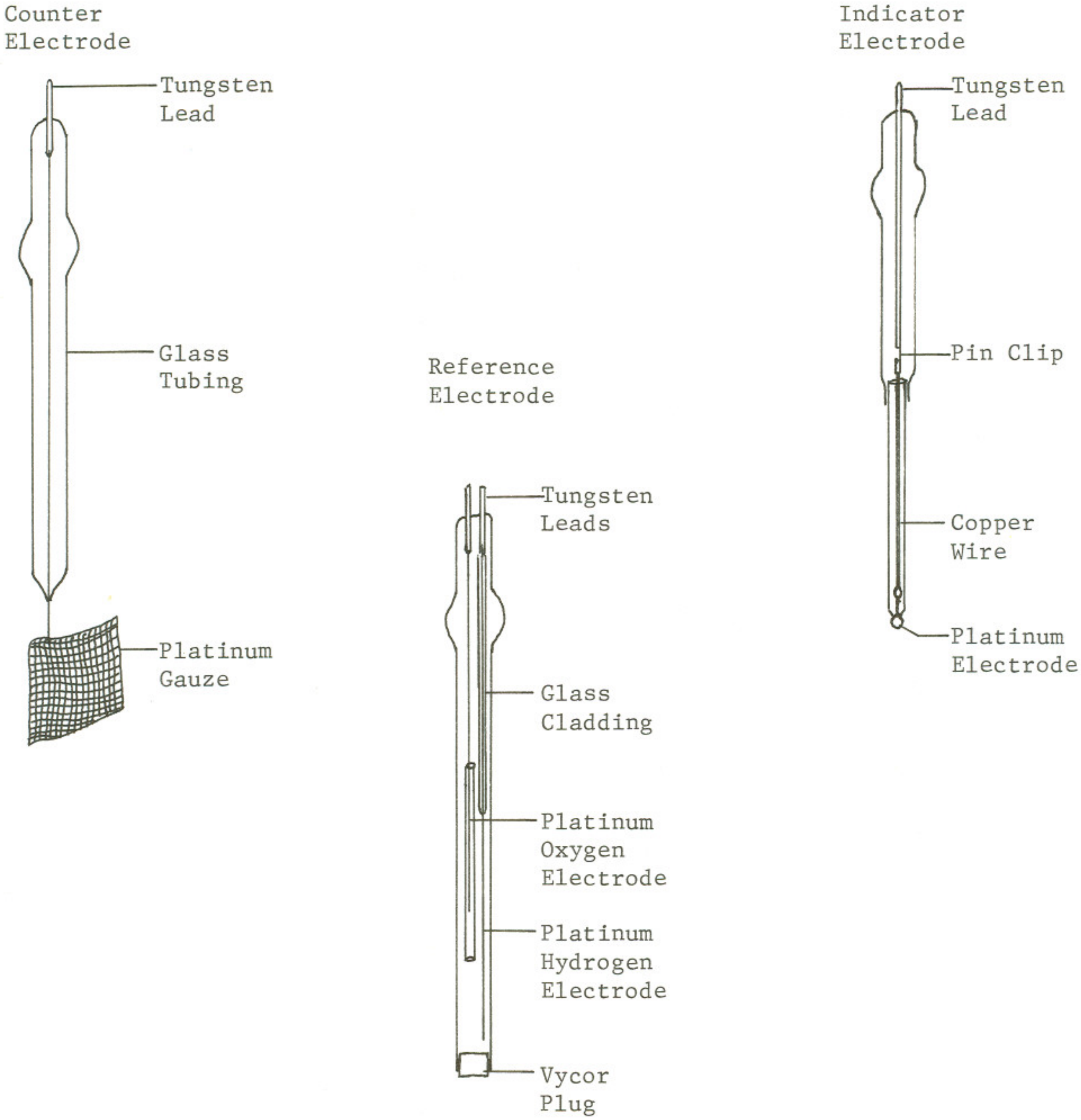


Figure 8
Detail of Electrodes

IV. DATA

Shown in Figure 9 is an example of a linear potential scan-current curve between 0 volts and 1.7 volts. The hydrogen adsorption region extends from approximately 0.4 volts to nearly 0.0 volts and includes the two maxima that are usually seen in this voltage range. The double layer region extends from about 0.4 volts to the beginning of the oxygen region at 0.8 volts with the oxygen region covering the remainder of the curve up to approximately 1.6 volts.

Figure 10 is an expanded curve of the hydrogen region. The curve was spread out by being recorded on a time axis and was started at 0.55 volts. The second trace in figure 10 is the current integration curve and gives the total area under the current potential curve up to any given potential. This integration can be used to obtain the total number of coulombs passed through the indicator electrode at any point along the curve.

Given in Tables I and II are data points from the coulomb curve for the various pressures at which data were taken. The individual data points were taken at the maxima and minima along the current-potential curve. The potentials given for the points are relative to an arbitrarily chosen point near the beginning of the hydrogen region. The numbers given are $\overline{x}$ and s, the average value of the set of raw data points, and the standard deviation of that set, respectively. All the values in the tables have been normalized to unit area. The area of each electrode is given at the top of the table. The relative potentials at which the data were taken are at the top of each column and the number of data from which the average values were obtained is given as N. Figures 11 through 14 are plots of the data in Tables I and II.

The results of the t-test for significance of difference done on the values in Table II are given in Table III. The t-test was not done for Table I since there was a very small number of data from which the average values were obtained. In Table II, the t-test was not done for the pressure change of 26mm Hg. -0.1 atm. since it was felt that extraneous, nonstatistical, fluctuations were responsible for the differences found. Given in Table III are: N, the number of points averaged, s, the standard deviation of the set, t, the number calculated from the t-test equation, and P, the probability that the differences found were significant. The equation used to calculate "t" is found at the bottom of the table.

Table IV is a table of the calculated values of the equilibrium constant K, and ΔG, the Gibbs free energy of adsorption. These values were calculated at constant coverage values for changes in system pressure.

The roughness factor was calculated for Electrode II at various times during use. The way in which this was done was to compare the hydrogen adsorption values obtained at full electrode coverage with what would be expected for a perfectly smooth electrode. The coulomb values and the roughness factors are listed in Table V.

Data taken from the coulomb curve for varying temperatures are found in Table VI. Figure 15 is a plot of these data.

Figure 16 is a drawing of the potential scan-stop measurements. Data taken from these curves for the "steady state" hydrogen desorption current are found in Table VII and a plot of these numbers is in Figure 17.

TABLE I   Coulomb Values at Varying Pressures and Potentials

Electrode I   Area= 6.25 mm^2

Cathodic Charge   ($\mu C/cm^2$)

		162.5mv	220mv	287.5mv	325mv	350mv
0.1 atm.	$\overline{X}$	108	204	356	437	501
N=2	s	3.95	3.39	5.67	6.22	14.14
1 atm.	$\overline{X}$	104	200	351	431	495
N=3	s	1.77	4.40	4.16	4.86	2.40
9 atm.	$\overline{X}$	145	252	449	550	624
N=4	s	6.18	24.6	36.1	43.2	44.6

Anodic Charge   ($\mu C/cm^2$)

		100mv	162.5mv	212.5mv	287.5mv	350mv
0.1 atm.	$\overline{X}$	30.0	93.9	168	279	415
N=2	s	2.82	6.22	2.83	2.83	8.48
1 atm.	$\overline{X}$	31.2	97.9	170	292	402
N=3	s	0.8	2.58	4.24	5.31	29.9
9 atm.	$\overline{X}$	38.1	122	220	391	547
N=4	s	1.22	2.11	2.77	5.2	11.4

TABLE II Coulomb Values at Varying Pressures and Potentials

Electrode II Area = 6.59mm^2

Cathodic Charge ($\mu C/cm^2$)

		162.5mv	220mv	287.5mv	325mv	350mv
26mm Hg	$\overline{X}$	86.3	153	252	312	357
N=8	s	5.58	10.7	14.5	12.2	12.0
0.1 atm.	$\overline{X}$	83.5	148	247	308	354
N=18	s	6.01	12.7	12.9	17.0	17.2
1 atm.	$\overline{X}$	87.3	153	255	318	363
N=29	s	9.28	11.3	12.5	13.5	14.8
9 atm.	$\overline{X}$	101	172	274	339	388
N=13	s	16.7	23.4	29.3	32.4	31.7
9 atm. (corr.)	X	97.3	162	269	339	390

Anodic Charge ($\mu C/cm^2$)

		100mv	162.5mv	212.5mv	287.5mv	350mv
26mm Hg	$\overline{X}$	54.0	109	164	252	332
N=8	s	20.3	22.5	23.4	23.1	24.6
0.1 atm.	$\overline{X}$	40.8	98.3	153	241	322
N=18	s	13.8	19.1	20.8	24.7	24.1
1 atm.	$\overline{X}$	37.6	94.5	152	246	333
N=29	s	11.2	17.8	21.1	23.1	28.5
9 atm.	$\overline{X}$	30.8	84.2	143.1	234	319
N=13	s	10.8	18.4	21.4	24.6	30.2
9 atm. (corr.)	X	27.3	84.2	139	236	324

TABLE III Significance of Difference t-Test*

Cathodic Charge μC (non-normalized)

		162.5mv	220mv	287.5mv	325mv	350mv
0.1-1 atm.	s(0.1)	0.396	0.885	0.840	1.12	1.14
	s(1)	0.612	0.746	0.821	0.891	0.978
N(0.1)=18	$\overline{X}(0.1)$	5.50	9.76	16.3	20.3	23.4
N(1) =29	$\overline{X}(1)$	5.75	10.1	16.8	21.0	24.0
	t	1.52	1.39	1.91	2.29	1.90
	P	86%	82%	94%	97%	94%
1-9 atm.	s(1)	0.612	0.746	0.821	0.891	0.978
	s(9)	1.10	1.54	1.93	2.14	2.09
N(1) =29	$\overline{X}(1)$	5.75	10.1	16.8	21.0	24.0
N(9) =13	$\overline{X}(9)$	6.66	11.1	18.1	22.3	25.6
	t	3.66	3.15	3.25	3.12	3.62
	P	99.9%	99.5%	99.5%	99.4%	99.9%

Anodic Charge μC (non-normalized)

		100mv	162.5mv	212.5mv	287.5mv	350mv
0.1-1 atm.	s(0.1)	0.911	1.26	1.37	1.63	1.59
	s(1)	0.737	1.17	1.39	1.52	1.88
N(0.1)=18	$\overline{X}(0.1)$	2.69	6.48	10.1	15.9	21.2
N(1) =29	$\overline{X}(1)$	2.48	6.23	10.0	16.2	21.9
	t	0.867	0.691	0.720	0.640	1.38
	P	63%	55%	57%	48%	81%
1-9 atm.	s(1)	0.737	1.17	1.39	1.52	1.88
	s(9)	0.713	1.21	1.41	1.62	1.99
N(1) =29	$\overline{X}(1)$	2.48	6.23	10.0	16.2	21.9
N(9) =13	$\overline{X}(9)$	2.03	5.55	9.43	15.4	21.0
	t	1.85	1.73	1.29	1.48	1.46
	P	88%	87%	79%	84%	84%

$$t = \frac{\{\overline{X}(1) - \overline{X}(2)\}}{\sqrt{\frac{\{N(1) - 1\}S(1)^2 + \{N(2) - 1\}S(2)^2}{N(1) + N(2) - 2}}} \sqrt{\frac{N(1)N(2)}{N(1) + N(2)}}$$

* For tables of values of t and P see Fisher and Yates (30).

TABLE IV Equilibrium Constant at Constant Coverage

Coverage = $335 \mu C/cm^2$

System Pressure	0.1 atm.	1 atm.	9 atm
K	2.69×10^{-3}	1.06×10^{-3}	5.2×10^{-2}
ΔG (Kcal/mole)	3.49	4.05	4.47

Coverage = $284 \mu C/cm^2$

System Pressure	0.1 atm.	1 atm.	9 atm.
K	7.33×10^{-3}	2.84×10^{-3}	1.12×10^{-3}
ΔG (Kcal/mole)	2.91	3.47	4.01

Coverage = $236 \mu C/cm^2$

System Pressure	0.1 atm.	1 atm.	9 atm.
K	1.89×10^{-2}	7.46×10^{-3}	3.28×10^{-3}
ΔG (Kcal/mole)	2.34	2.89	3.38

Coverage = $190 \mu C/cm^2$

System Pressure	0.1 atm.	1 atm.	9 atm.
K	5.10×10^{-2}	1.90×10^{-2}	7.90×10^{-3}
ΔG (Kcal/mole)	1.76	2.34	2.86

TABLE V Calculation of Roughness Factors During Use

Electrode II Full coverage at $210 \mu C/cm^2$ [8]

Date of Scan	10-12-72	10-26-72	11-2-72
Cathodic Charge	$345 \mu C/cm^2$	$357 \mu C/cm^2$	$368 \mu C/cm^2$
Roughness Factor	1.64	1.70	1.75

TABLE VI Changes in Current With Changing Temperature

Electrode II

Cathodic Charge $(\mu C/cm^2)$

		162.5mv	220mv	287.5mv	325mv	350mv
47°C	$\overline{X}$	74.1	142	239	309	365
	s	1.91	3.15	3.47	4.93	10.4
24°C	$\overline{X}$	87.0	154	258	327	375
	s	0.44	0.88	0.44	0.44	0.44
14°C	$\overline{X}$	97.1	163	268	334	380
	s	6.98	5.78	6.51	5.98	7.53

TABLE VII Steady State Hydrogen Evolution Current

Electrode II

Cathodic Current μA (non-normalized)

		332mv	220mv	107mv	69mv	56mv
1 atm.	X	0.9	0.4	0.2	0.1	0.05

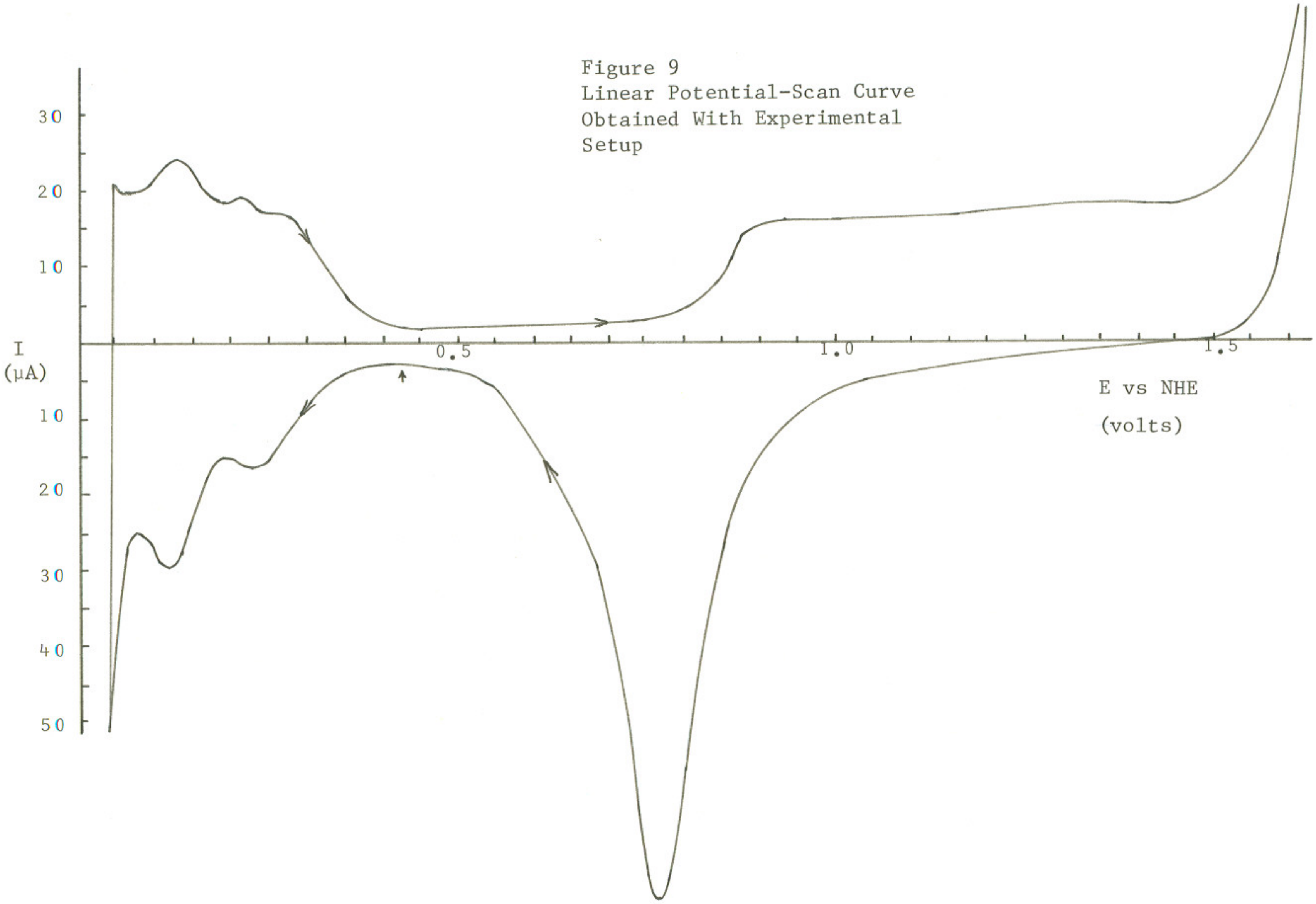
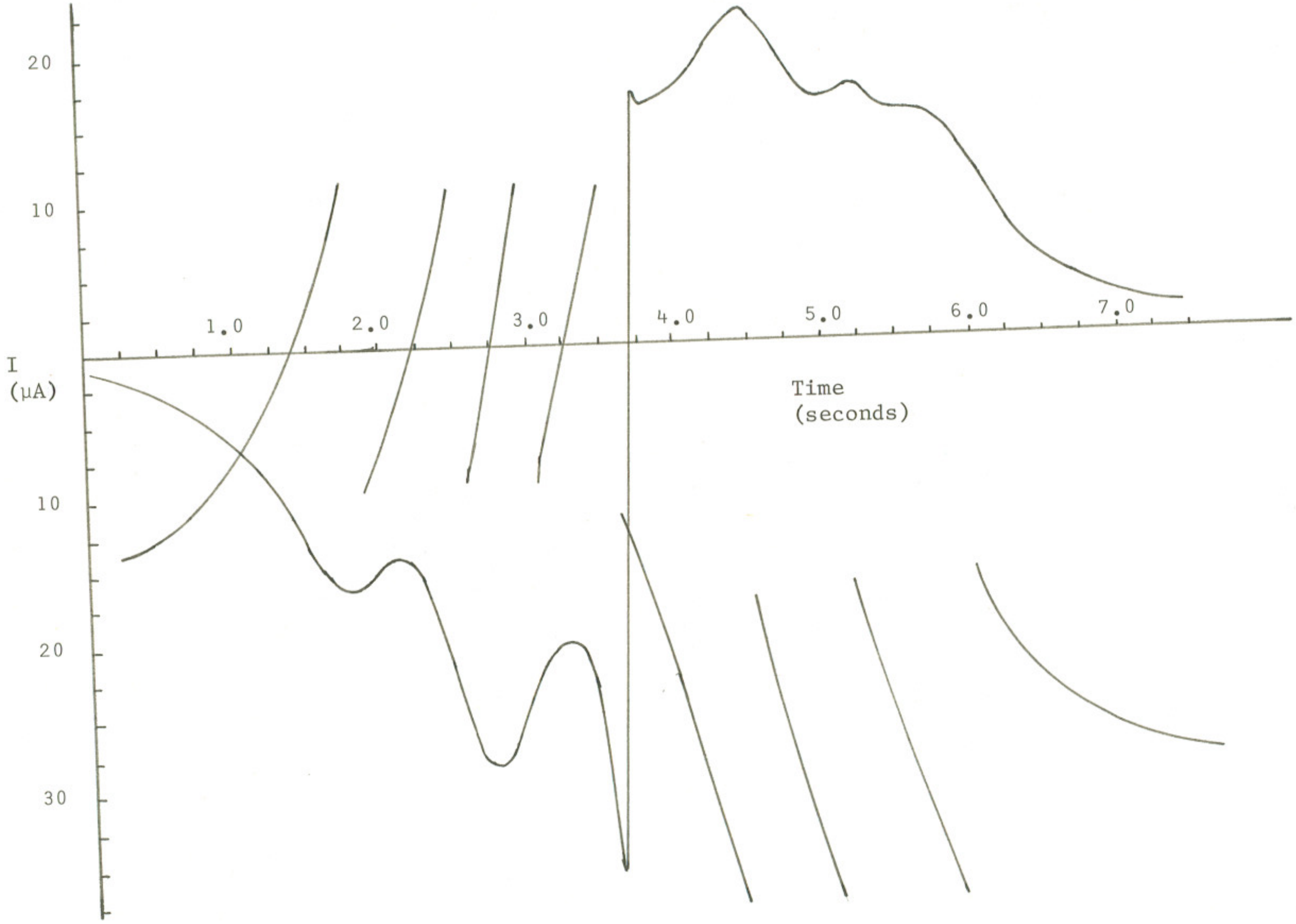


Figure 9
Linear Potential-Scan Curve
Obtained With Experimental
Setup

Figure 10
Expanded Curve Over The
Hydrogen Region



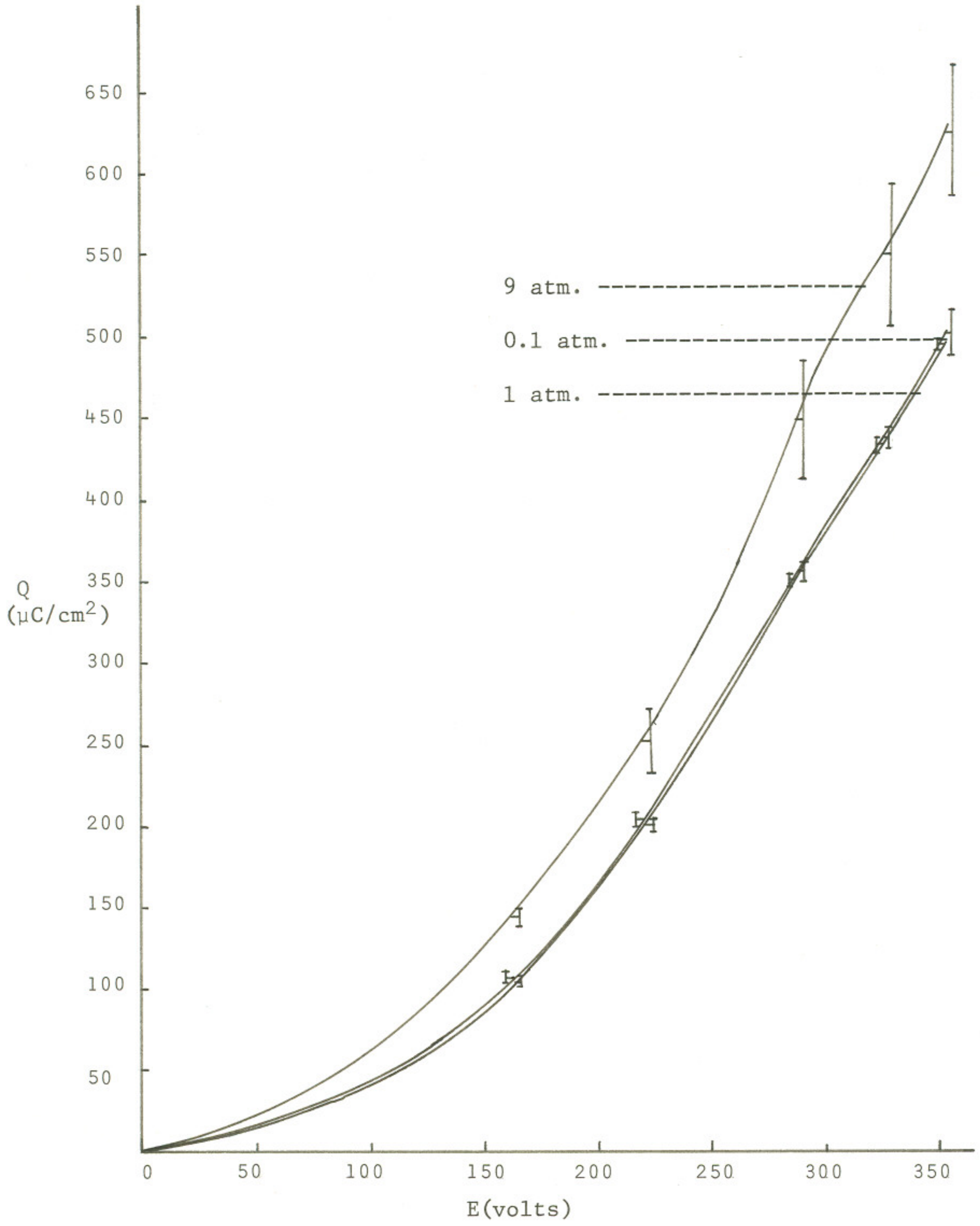


Figure 11
Coulomb Curve
Cathodic Electrode I

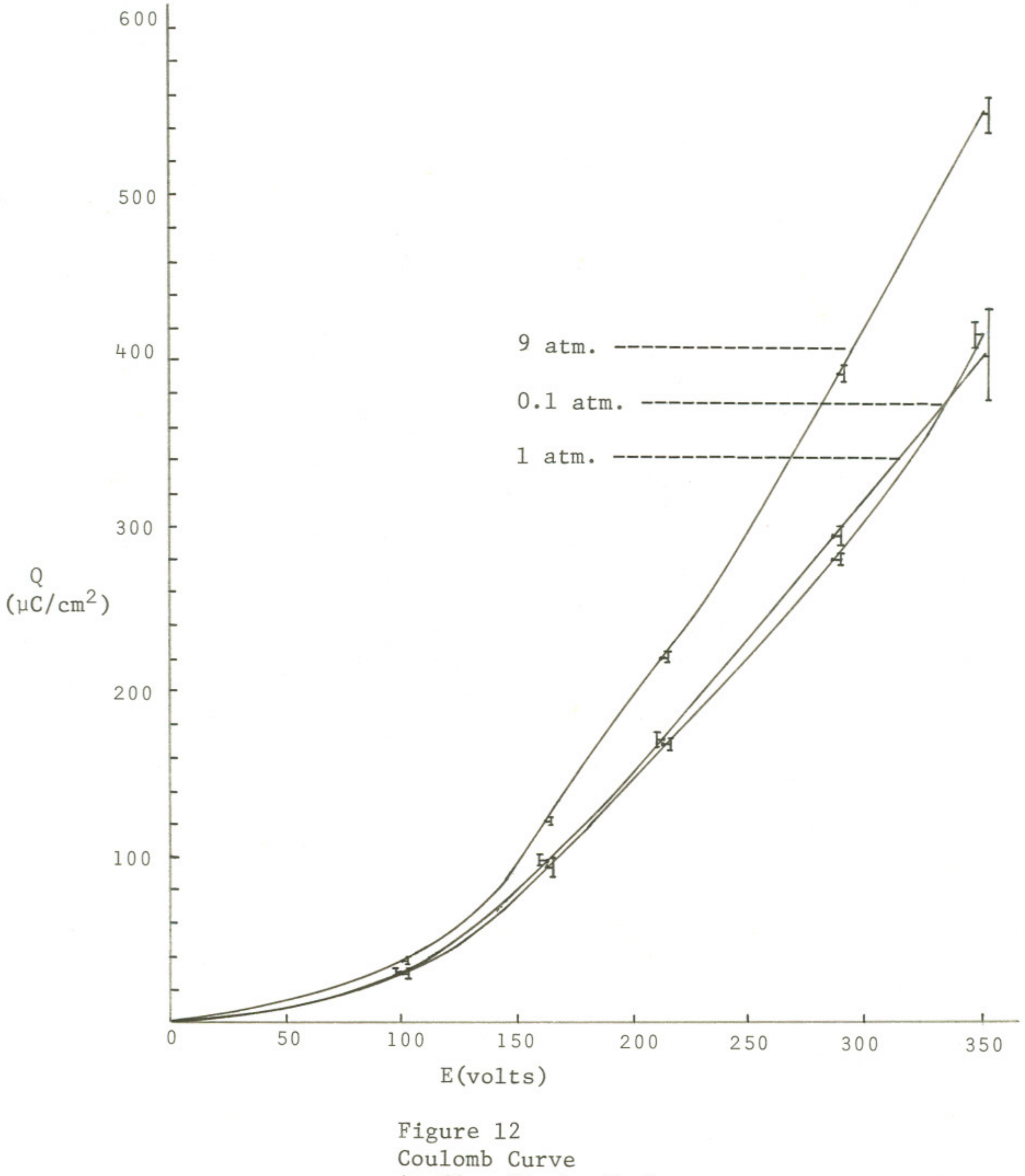


Figure 12
Coulomb Curve
Anodic Electrode I

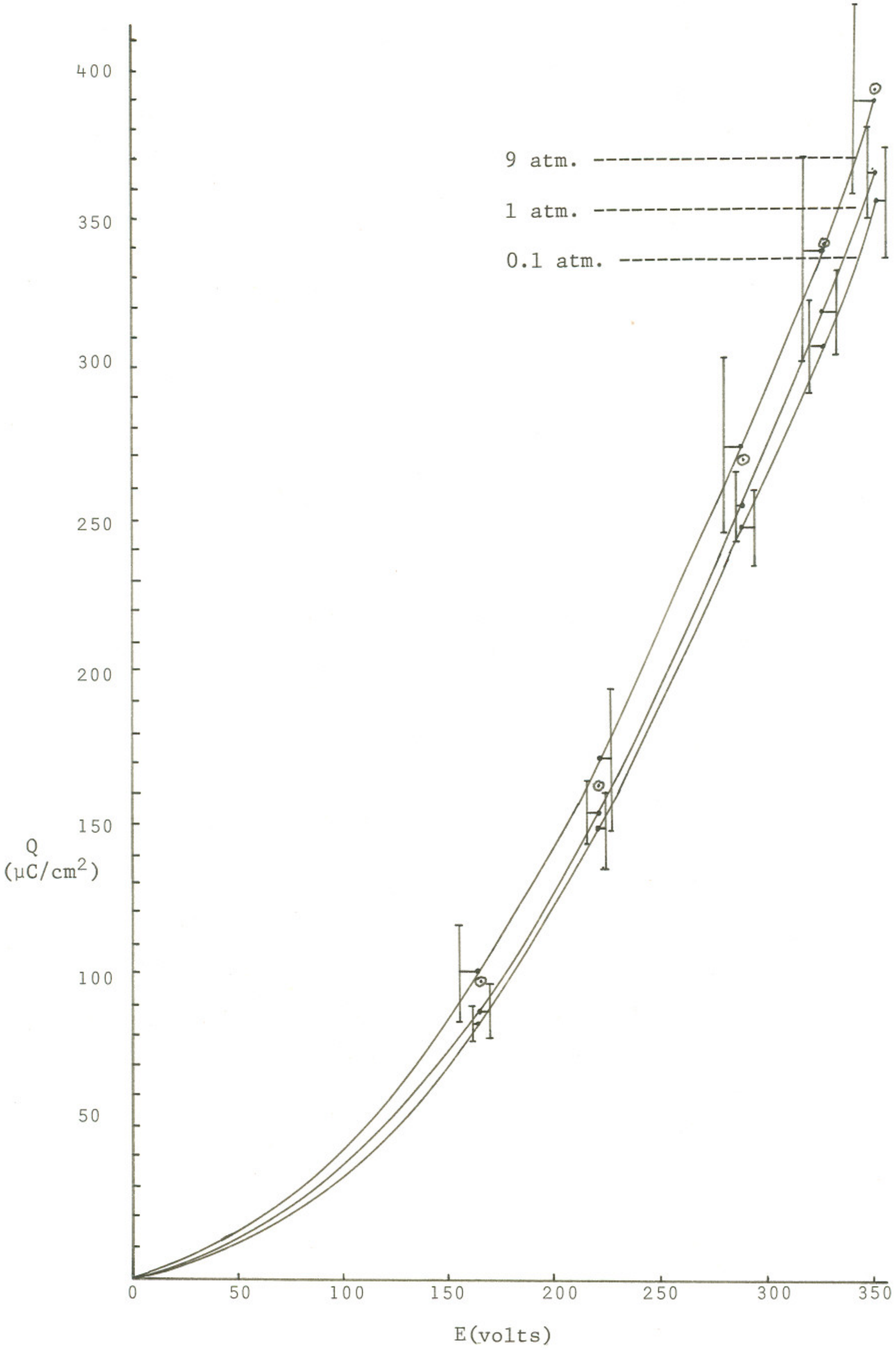


Figure 13
Coulomb Curve
Cathodic Electrode II

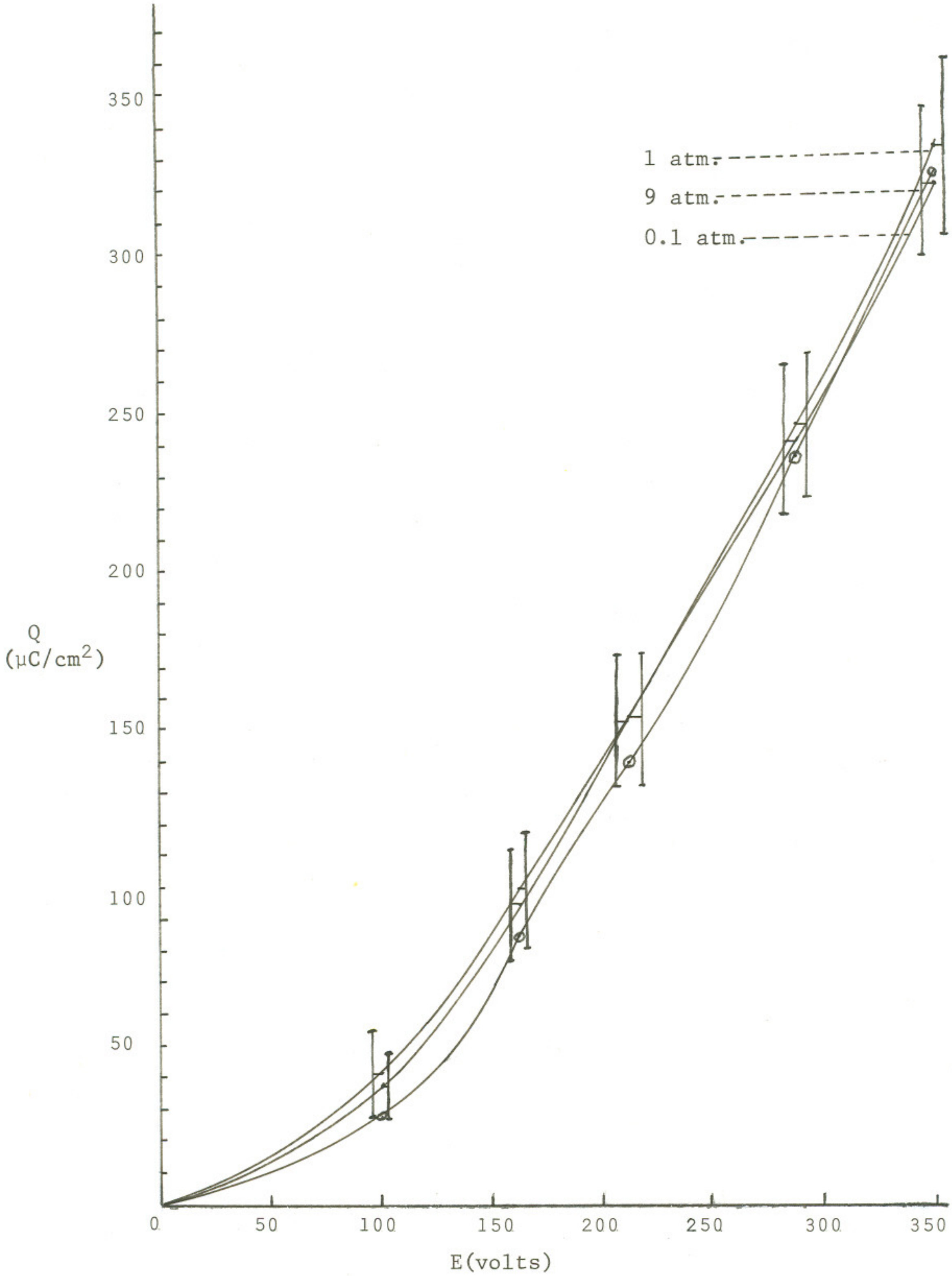


Figure 14
Coulomb Curve
Anodic Electrode II

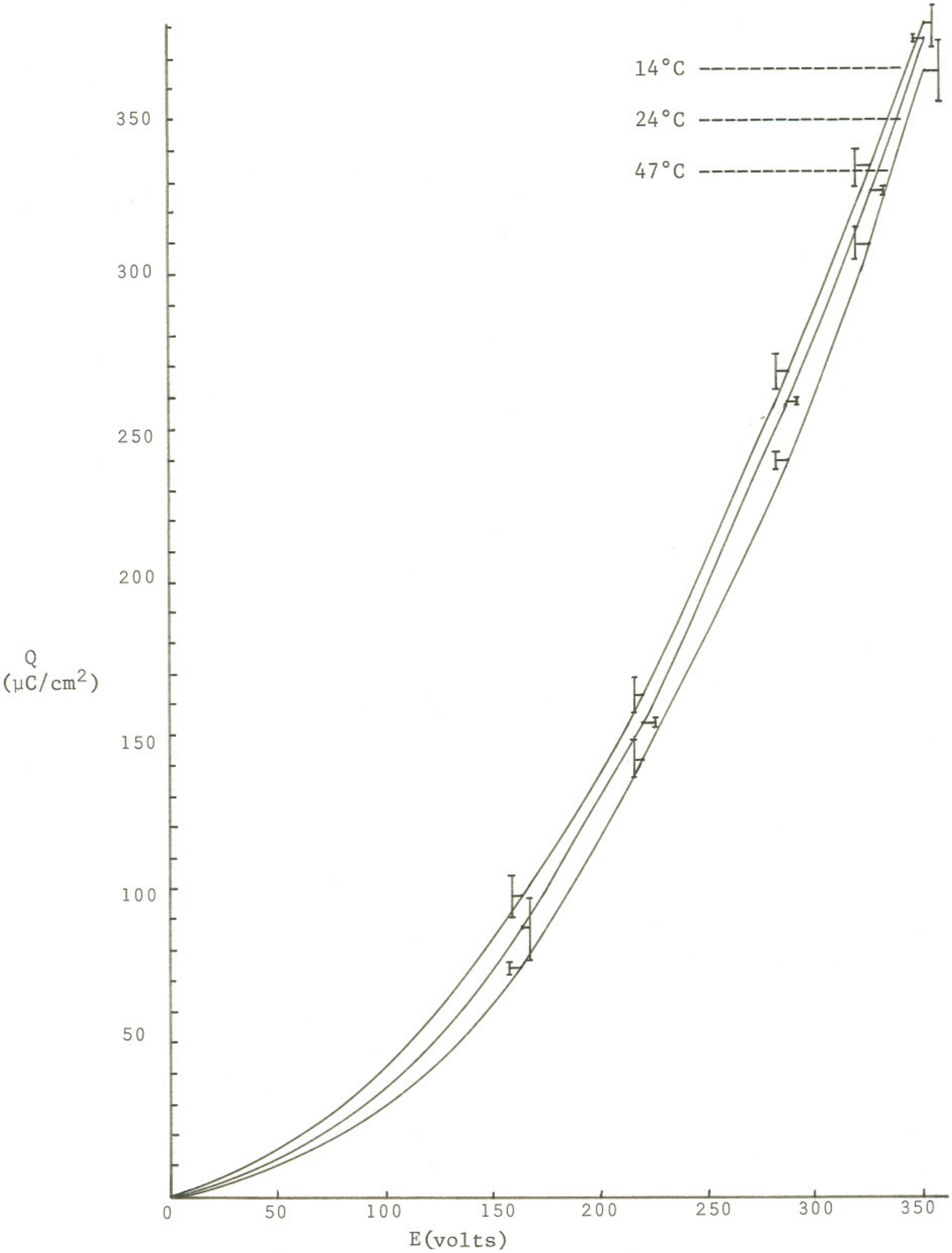
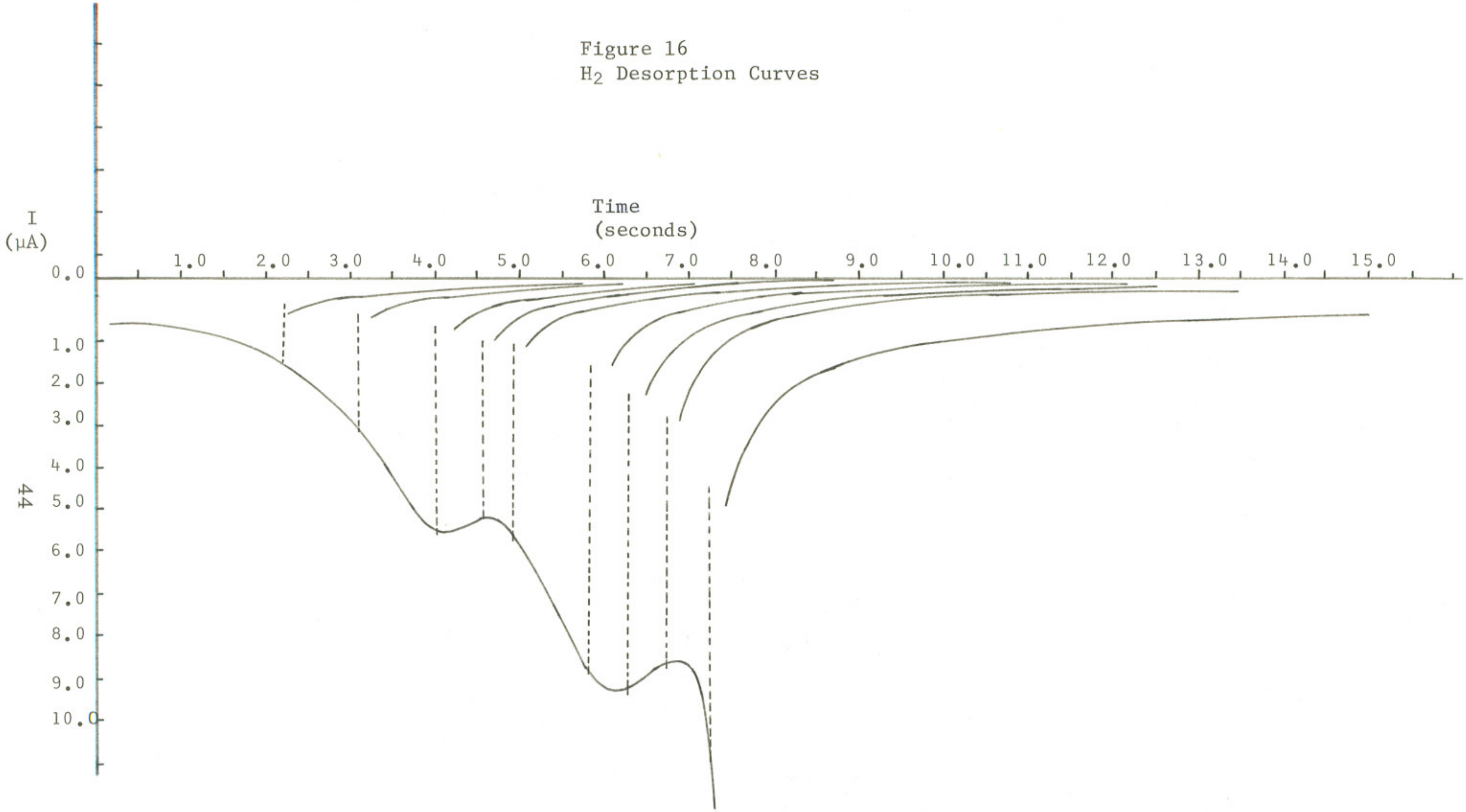


Figure 15
Coulomb Variations
With Temperature

Figure 16
H_2 Desorption Curves



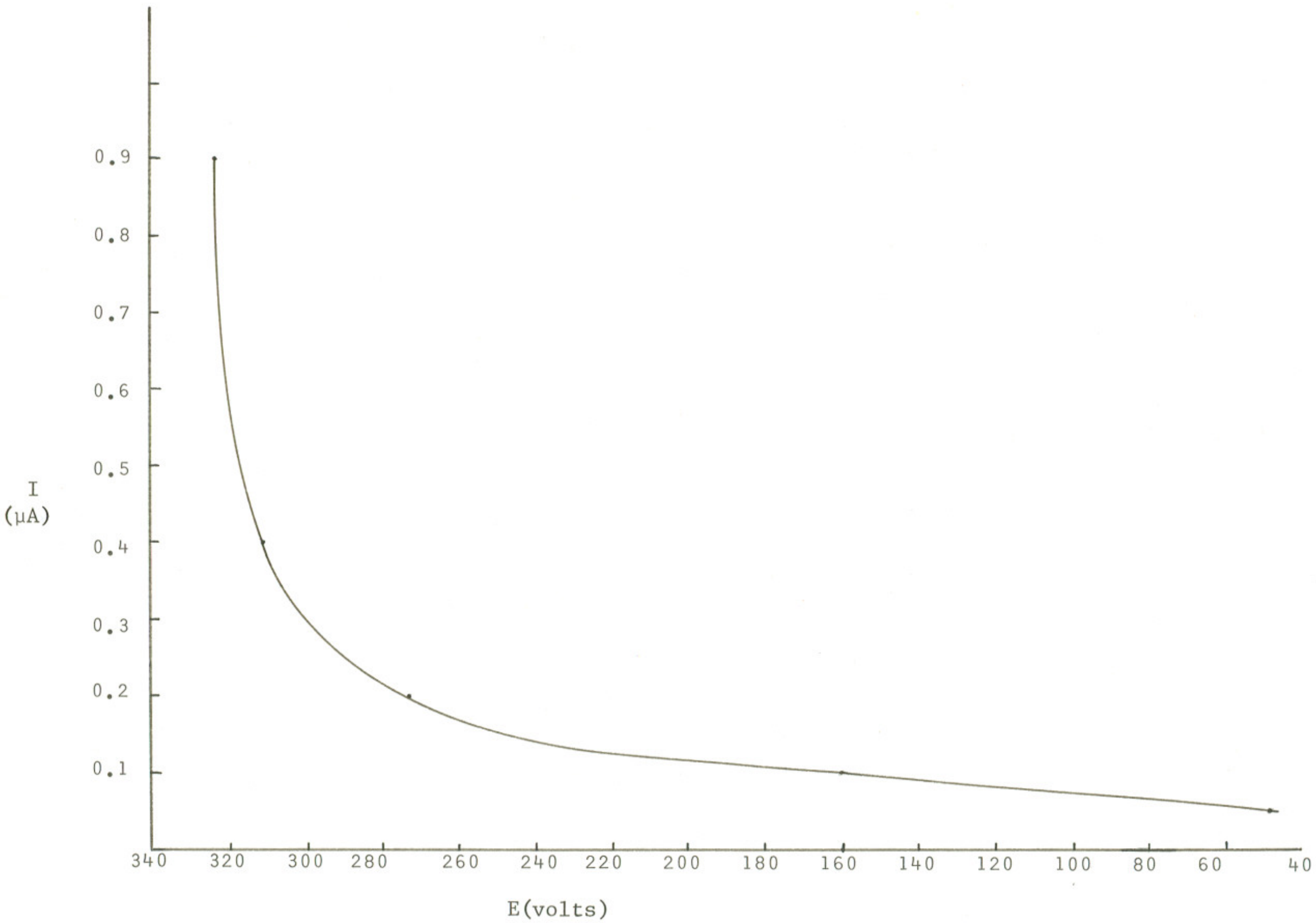


Figure 17
Steady State H_2 Evolution

V. DISCUSSION

According to the Langmuir theory, adsorption of a gas on a metal surface is pressure dependent. The basis for this is the pressure dependence of the collision frequency of the adsorbed molecules as well as the "sticking coefficient" of these molecules. If it is assumed, as has been in the past, that there is full coverage at one atmosphere pressure, then increased pressure would not affect the hydrogen uptake values unless secondary layers of hydrogen were being built up. If the "sticking coefficient" of hydrogen is sufficiently low on a metal surface surrounded by solution, it might then be assumed that there is only a partial monolayer of hydrogen on the electrode. If this held true up to a partial hydrogen pressure of one atmosphere then a full coverage would not be attainable before the hydrogen was bubbled away from the electrode. If this is the case, then an increase in pressure will make available higher pressures of hydrogen at the electrode surface before bubble formation occurs.

According to the Nernst equation, with thirty millivolt increase in the electrode potential there is a tenfold increase in the hydrogen partial pressure at the electrode-solution interface. By increasing the pressure of the system a wider range of potentials is made available for study before violent hydrogen evolution occurs. With this extended range, it becomes possible to observe adsorption over an increased potential region.

Examination of the data in Tables I and II will show that there was a pressure dependence observed in the hydrogen adsorption values. Figures 11 through 14 are plots of these data. In the original current-potential curves it was seen that instead of the curve being extended by thirty millivolts as expected, the entire curve was shifted by this amount. The plots of Figures 11-14 are all referenced to the peaks and valleys of the current-potential curve and are not shifted as they should be. Under these conditions it is seen that, for any given potential, the hydrogen adsorption values increase with increasing pressure. If these curves are plotted with the appropriate changes for the 0.1 and the 9 atmosphere curves the order of the curves seen in Figures 11-14 is reversed. At a point of constant hydrogen partial pressure on three curves the order of hydrogen adsorption values is 0.1 atm >1 atm >9 atm. When values of K, the equilibrium constant, and ΔG, the Gibbs free energy of adsorption, are calculated from these curves at constant hydrogen coverage, it is seen that there is a positive change in ΔG as the system pressure is increased. The values for this calculation are found in Table IV. Using the Maxwell relation it is seen that increased pressure corresponds to a more negative value of entropy. This result might be expected since at lower coverages the change in entropy would be lower. Since further interpretation of these curves have not been completed, the remainder of the discussion will concern the curves as they are plotted in Figures 11-14.

Returning to Tables I and II it is seen that there are two anomalous points among the data. The discrepancy of the odd point in Table I has been attributed to statistical fluctuations in the small set of data from which the average value was obtained.

The decrease in current from 0.1 to 1 atmosphere is approximately 1% of the total value while the increase in current from 1 to 9 atmospheres is an increase of 25%. While the first difference is easily accountable to statistics of a small sample, the latter one might be more indicative of a true change in the system.

The second anomalous point, at 26 mm of mercury in Table II can also be related to statistical causes. Measurements at pressures below 0.1 atmosphere were not started until late in the study of Electrode II. As can be seen in Table III, the roughness factor (the ratio of true surface area to geometric surface area) of the electrode increased over the course of the experiment. (It should be noted here that the roughness factor is calculated using a theoretically determined surface area for a perfectly smooth electrode and comparing it with the surface area of any given electrode). The true surface area of the electrode is determined by use of the hydrogen adsorption values at full coverage while the theoretical adsorption values are calculated from the geometric surface area. Although it might be possible to statistically compensate for this change in surface area, the uncertainty in the result would make this procedure pointless.

In order to determine confidence levels for the data, a t-test for significance of difference was done on the coulomb values for Electrode II.

The t-test was omitted for Electrode I due to the small number of data obtained in the study of its pressure dependence. As can be seen from the results of the t-test, there is a very high probability that the differences observed in the data are true variations in the system.

Such is not the case for the anodic currents recorded. In Table I there is an indication that the anodic current has increased with pressure. This trend is not carried out in the values obtained in Table II. The differences in the final uptake values for the three presumably valid pressures is less than 5% of the total uptake figure. As might be expected, the probabilities from the t-test for the anodic currents are considerably lower than those obtained for the cathodic currents.

While trying to validate these unexpected results it was discovered that the entire curve was, at times, offset anodically or cathodically depending on whether the pressure was increased or decreased from its equilibrium value at one atmosphere. It was also noted that the increase was not always apparent in the 9 atmosphere curve. The effect of the shift of the curve at higher pressures was to increase the cathodic current and decrease the anodic current. In order to check the possibility that this shift was responsible for all the differences observed, a curve at 9 atmospheres was picked that didn't show any appreciable shift. The data points from this curve are found in Table II as the 9 atm. (corr.) points. It is seen that the cathodic current values obtained for this curve are within a few percent of the average values obtained. The anodic current figures are slightly higher than the average values obtained at 9 atmospheres but they are still very nearly equal to those figures found for the lower pressures.

There were two explanations proposed for the curve offset. The first possibility was that the increased pressure allowed a higher concentration of dissolved oxygen to be present at the solution-electrode interface. The oxygen dissolved into the solution after being generated in the anodic cleaning procedure and, at a more cathodic potential, diffused back to the electrode surface and was reduced. The second proposed mechanism was that the increased pressure of the system allowed a much more highly oxidizing atmosphere at the electrode surface when the electrode was anodically cleaned. This opened the possibility either for a different, and more stable, type of oxide layer to be formed on the electrode surface or for oxygen to diffuse into the bulk of the electrode.

In either case the oxygen would remain present at the electrode surface even after the normal oxygen reduction potential had been passed. A study was made to try to determine which, if either of these mechanisms was operative but no results were obtained in the time that was available.

Since the adsorption curves are dependent on temperature, as has been shown by Bold and Breiter[27], it was decided to see if the differences observed in our system might have been caused by variations in the ambient temperature. The results of this study are found in Table V. As was expected there was an appreciable increase in the adsorption current with decreasing temperature.

It is also apparent that the change in adsorption current over a twenty degree temperature range would not account for the observed differences in adsorption for the various pressures. A plot of the variations observed is seen in Figure 15.

Returning to the data in Tables I and II it should be noticed that not only is the pressure dependence that is exhibited in the cathodic branch of the curve absent in the anodic, but also, the cathodic current is always larger than the anodic. The explanation of this problem, at present is not entirely complete.

The possible mechanisms available to the hydrogen atom after it has been adsorbed are limited to one, or a combination, of three possible means of leaving the surface of the electrode. The first and most likely method of escape is for the atom to regain its positive charge on the anodic sweep and return to the solution as an ion. The second possibility is for the hydrogen atom to diffuse into the bulk of the electrode. The third avenue open to the atom is for it to combine with another hydrogen atom and dissolve into the electrolyte.

The first of the above mechanisms is producing the anodic current and is acting as expected in this system. One or possibly both of the other two mechanisms are thought to be responsible for the difference observed between the anodic and cathodic current.

The movement of the hydrogen atom into the bulk of the electrode would be governed by Fick's laws of diffusion. The hydrogen atoms would be random walking from a point of high concentration to a point of lower concentration inside the bulk of the electrode. The driving force for the desorption of hydrogen gas is a more complex phenomenon. As already mentioned, the partial pressure of hydrogen in the solution layer just outside the surface of the electrode is governed by the Nernst equation. The Nernst equation states that there must be a specific partial pressure of hydrogen gas around the electrode and that this pressure must correspond to the potential of that electrode. Since the potential is being scanned at a finite rate, the hydrogen partial pressure must change at the electrode-solution interface to maintain the equilibrium dictated by the Nernst equation. Since the partial pressure of hydrogen in the solution is maintained at a low level by constant bubbling of helium, it must be assumed the direction of hydrogen flow is from the electrode to the solution. The hydrogen at the electrode surface will be on a concentration gradient and will diffuse away from the solution layer surrounding the electrode. What will be observed, then, will be a constant diffusion of hydrogen away from the electrode until its potential is in equilibrium with the hydrogen layer generated around the surface. This hydrogen will be lost to the solution and will not be oxidized with the hydrogen that has remained on the surface of the electrode.

Both of the above processes are pressure dependent. The diffusion of hydrogen atoms into the platinum will depend on the pressure since the density, or concentration, of hydrogen atoms at which the hydrogen gas will bubble away from the electrode will increase with higher pressures.

The desorption process is, again, more complex. Since the pressure of the system is increased, the partial pressure of hydrogen at the electrode will be able to attain a higher value before saturation occurs. Since there is an increase in the partial pressure of hydrogen at the electrode surface, the concentration gradient of the dissolved hydrogen will be able to attain a higher value. Another result of increased pressure on the system is that the solubility of the hydrogen in the electrolyte is increased.

In order to see which, if either, of these mechanisms was taking place, a potential scan-stop study was made. It was felt that this type of measurement would yield a hydrogen desorption curve. As can be seen in Figure 16, the potential was scanned up to a chosen voltage at which the scan was stopped. The recorder was operated in the time mode and was allowed to continue as the current decayed after cessation of the potential sweep. The result was a logarithmic decay curve. Unfortunately, the response time of the recorder was not fast enough to give values at short times after the scan-stop, so extrapolated values were obtained. Oscillographic traces were also made to try to increase the reliability of the short time values but the time available was not adequate to perfect this technique. In a number of cases the time scan was continued over a period of seconds to give a "steady state" hydrogen evolution curve. A set of typical values for this current is found in Table VI and their plot in Figure 17.

Since measurements of this type have not been made before, an analysis of these curves should prove very useful in determining the mechanisms that are causing the desorption current.

If the concentration gradients can be determined for the hydrogen gas in the solution and the hydrogen atoms in the bulk platinum, it might then be possible to calculate the diffusion coefficients from the experimentally observed decay curves. These could then be compared with the diffusion coefficients of hydrogen in water and atomic hydrogen in platinum that have already been tabulated.

In conclusion, it can be said that there is a definite pressure dependence present in the hydrogen region of the potential curve which has, until now, never been observed. It is apparent that appreciable amounts of hydrogen are lost from the electrode surface and that this loss is pressure dependent. Further study on the time decay curves will be necessary to determine the exact origin of the hydrogen loss. Future analysis will also have to be done to determine the causes of the pressure dependent offset of the hydrogen region of the potential curves.

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