

70-17,788

MILLER, Gail Edwin, 1933-  
INVESTIGATION OF THE OXYGEN FILMS ON PLATINUM  
ELECTRODES.

University of Arizona, Ph.D., 1970  
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan

INVESTIGATION OF THE OXYGEN FILMS  
ON PLATINUM ELECTRODES

by

Gail Edwin Miller

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A Dissertation Submitted to the Faculty of the  
DEPARTMENT OF CHEMISTRY  
In Partial Fulfillment of the Requirements  
For the Degree of  
DOCTOR OF PHILOSOPHY  
In the Graduate College  
THE UNIVERSITY OF ARIZONA

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Gail Edwin Miller entitled Investigation of the Oxygen Films on Platinum Electrodes be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

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*Paul E Miller*

## ACKNOWLEDGMENTS

The author wishes to thank his advisor, Dr. Louis Ramaley, for his guidance throughout this work and specifically for his assistance on instrumentation problems.

The author would also like to acknowledge his wife, Dree, and his children, whose patience and sacrifices made this dissertation possible.

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## ABSTRACT

The main goal of this research was to investigate the properties of oxygen films on platinum electrodes formed by anodization between  $\pm 0.80$  and  $2.50$  V (vs. N.H.E.).

The oxygen films were formed by potentiostatic anodization of a platinum electrode for 30 sec in deaerated  $0.5$  F sulfuric acid. The electrode had been pretreated by repetitive ac cycling between  $0.01$  and  $1.40$  V to remove pre-existing oxygen films and surface contaminants. The oxygen films were removed by two different methods: chemical dissolution and electrochemical reduction.

In the chemical dissolution of the oxygen films, the anodized electrodes were exposed to  $1$  F hydrochloric acid at  $85-95^{\circ}$  for one hour. Ultraviolet absorption spectra were obtained for these hydrochloric acid solutions, and the concentrations of the Pt(II) and Pt(IV) chloro-complexes were determined from these absorbance measurements. The molar ratio of Pt(II)/Pt(IV) was calculated for oxygen films formed by anodizations between  $1.15$  and  $2.35$  V. The molar ratio was 3 or 4 to 1 for the lowest potential anodization, and the values decreased gradually to about 2 or 3 to 1 for the highest potential studied. The amount of oxygen film removed by chemical dissolution was calculated from the charge equivalent to the sum of the two platinum ions. The amount of oxygen film increased linearly for anodizations between about  $1.00$  and  $2.00$  V with a limiting value of  $1.15$  mC/cm<sup>2</sup> being approached above  $2.00$  V. At  $1.15$  V, the lowest potential at which detectable amounts of

film were formed, the amount of oxygen film was  $0.226 \text{ mC/cm}^2$ . At 1.00 V, the chemical dissolution method gave inconclusive results because the UV absorbance of the hydrochloric acid solutions was too small. The extrapolated amount of film at 1.00 V was  $0.050 \text{ mC/cm}^2$  which was below the minimum detection limit of  $0.080 \text{ mC/cm}^2$  for this method.

The amount of oxygen film removed by electrochemical reduction (a potentiostatic transient at 50 mV/sec to 0.40 V) also increased linearly from 1.00 to 2.35 V with a limiting value of  $1.33 \text{ mC/cm}^2$  being approached above 2.00 V. The amounts of oxygen film determined by the two methods compared favorably for anodizations above 1.25 V. The electrochemical values were always higher, and the difference between the two sets of data was less than 20% of the electrochemical values. The difference was fairly constant at about  $0.080 \text{ mC/cm}^2$  for the lower potentials up to about 1.60 V and between 0.10 and  $0.20 \text{ mC/cm}^2$  above 1.60 V.

At 1.00 V the amount of oxygen film formed was  $0.107 \text{ mC/cm}^2$  by the electrochemical method but only about  $0.050 \text{ mC/cm}^2$  by the chemical dissolution method. The electrochemical reduction was performed by a cathodic transient beginning immediately after the anodization, while the chemical dissolution was started after a 2-min period required to remove oxygen from the dissolution cell. The loss of much of the oxygen film during this 2-min waiting period showed the possible presence of a weakly adsorbed platinum-oxygen species.

Previous investigators have published data and theories describing oxygen films which are not reduced by cathodic transients. If the reduction transient is not sufficiently cathodic, oxygen films will be

only partially reduced. Data were obtained to show that the oxygen film reduction peak can be shifted cathodically if experimental conditions are improperly chosen. Two previously known methods of moving the reduction peak to more cathodic potentials, increased sweep rate and increased anodization potential, were demonstrated. A new experimental condition which caused the oxygen film reduction peak to move cathodically was identified as the length of anodization time when the potential was above 1.95 V. The molar ratios of Pt(II)/Pt(IV) of these partially reduced oxygen films were the same as for oxygen films formed at the same potentials and not partially reduced.

It was concluded that chemical dissolution of oxygen films was a valid method of obtaining information. The data obtained by this method agreed reasonably well with data obtained by electrochemical reduction of oxygen films. An evaluation of previously published information concerning this method was presented to support this conclusion.

## INTRODUCTION

The problem of understanding the nature of the oxygen film on platinum electrode surfaces has occupied the attention of many research chemists for many years. Several notable points of controversy have eluded resolution despite the accumulation of great amounts of data using most of the electrochemical techniques for investigation. The magnitude of the effort that has been expended on this subject is illustrated by the review written by Gilman (1967). This review required 81 pages and listed 146 literature references. Like most reviewers, the author was forced to neglect certain aspects of his subject and, in some cases, to disregard some contributions altogether. In addition, several notable contributions have been made since Gilman's review was written. It is clear that no single document will completely and adequately describe the nature of the oxygen films which are formed on platinum electrodes.

In at least some cases, confusion instead of clarification has been the result because of experimental difficulties or poorly chosen experiments themselves. For example, the work of many researchers may be invalid because their work was performed in solutions containing minute traces of impurities. James (1967) and Gilman (1967, p. 112-118) present excellent descriptions of the precautions necessary to obtain data that will not be compromised and later discredited by others as being caused by reactions with impurities. Another major problem

has been the complete reliance upon electrochemical data by most investigators. Not enough use has been made of other means of obtaining data, such as chemical dissolution of the oxygen films, other chemical methods, and physical methods for examining thin films and metal surfaces.

Some of the confusion has resulted because experimental observations are subject to more than one explanation. For example, the amount of charge required to form the oxygen film is always larger than the charge consumed when the film is removed. A completely adequate model or description of the oxygen film must deal with this fact. Various mechanisms have been offered to at least partially explain this observation: (a) Laitinen and Enke (1960) and Shuldiner and Warner (1965) suggested that some of the oxygen atoms diffused from the electrode surface into the grain boundaries or beneath the surface layer and were not available for reduction during the cathodic transient, (b) Vetter and Berndt (1958) suggested that some of the oxygen in the film was reduced only to hydrogen peroxide which diffused away from the electrode and was not reduced to water, (c) Feldberg, Enke, and Bricker (1963) concluded that two different oxides were formed, one not reducible at the potentials employed, (d) Lauer (1967) also concluded that an electro-inactive oxide, mainly the Pt(IV) oxide, was formed, (e) Shibata (1964) suggested that oxygen deposited below 1.15 V (N.H.E.) was loosely attached and may have been lost spontaneously before it was reduced, and (f) the work of several investigators, including James (1967) and Feldberg et al. (1963), concluded that oxidation of

impurities contributed to the larger amounts of electricity required during the anodic transient as compared to the cathodic transient. This list does not include all of the proposed explanations, but it does illustrate the magnitude of the problem of explaining a rather simple experimental observation. Later investigators have criticized some of these explanations, but none has been successful in devising experiments of sufficient ingenuity to clearly discredit all alternatives and leave us with only one acceptable explanation.

In the following section the main experimental observations will be listed with explanations that are either generally accepted or have been advanced by leading authorities in this field of investigation. Unless otherwise stated, the data were obtained in oxygen-free acidic solutions, usually 0.5 F sulfuric or 1 F perchloric acid, with smooth platinum electrodes. Hereafter, all potentials are positive and are referred to the normal hydrogen electrode.

#### Existence of an Oxygen-containing Film on Platinum Surfaces

Platinum surfaces anodized above 0.8 V in aqueous acid solutions form an oxygen film whose nature has not been defined to everyone's satisfaction. The stability of this film was shown by Anson (1957) who observed that an oxidized platinum electrode which stood overnight in deaerated 1 F sulfuric acid still retained 80% of its original oxygen film. This oxygen film can also be formed using chemical oxidizing agents as shown by Anson and Lingane (1957), Every and Grimsley (1965), and Lauer (1967).

### Chemical Dissolution of the Film by Acidic Chloride Solutions

The oxygen film has been chemically removed from the electrode surface by hot NaCl-HCl and HCl solutions. Subsequent chemical analysis of these solutions by ultraviolet spectrophotometry showed that Pt(II) and Pt(IV) chloro-complexes were present. This led to the conclusion that the film contained both Pt(II) and Pt(IV) oxides in the same ratios as the observed chloro-complexes. This conclusion has been made by Anson and Lingane (1957), Every and Grimsley (1965), and Lauer (1967). It has been criticized mainly by Breiter and Weininger (1962).

### Shapes of the Anodic and Cathodic Current-voltage Curves

The shapes of the current-voltage curves are different for the formation and removal of the oxygen film as shown in Figure 1. Starting with a clean electrode only a minimal current flows between 0.4 to 0.8 V. This is known as the double-layer region in which the current flows only to charge the double-layer and to react with solution impurities. The oxygen sorption region is above 0.8 V. The potential at which appreciable current starts to flow is determined by several factors including solution impurities and electrode pretreatment (Breiter 1966 and Biegler 1967). At about 1.65 V, depending on several factors--mainly the acidity, a large increase in current accompanies the formation of gaseous oxygen. When an anodized electrode is cathodized at a slow sweep rate (e.g., 50 mV/sec), very little current is passed until the reduction peak is observed between 0.6 to 0.8 V. (Hereafter, the term "slow sweep rate" will mean a rate at which reduction peak



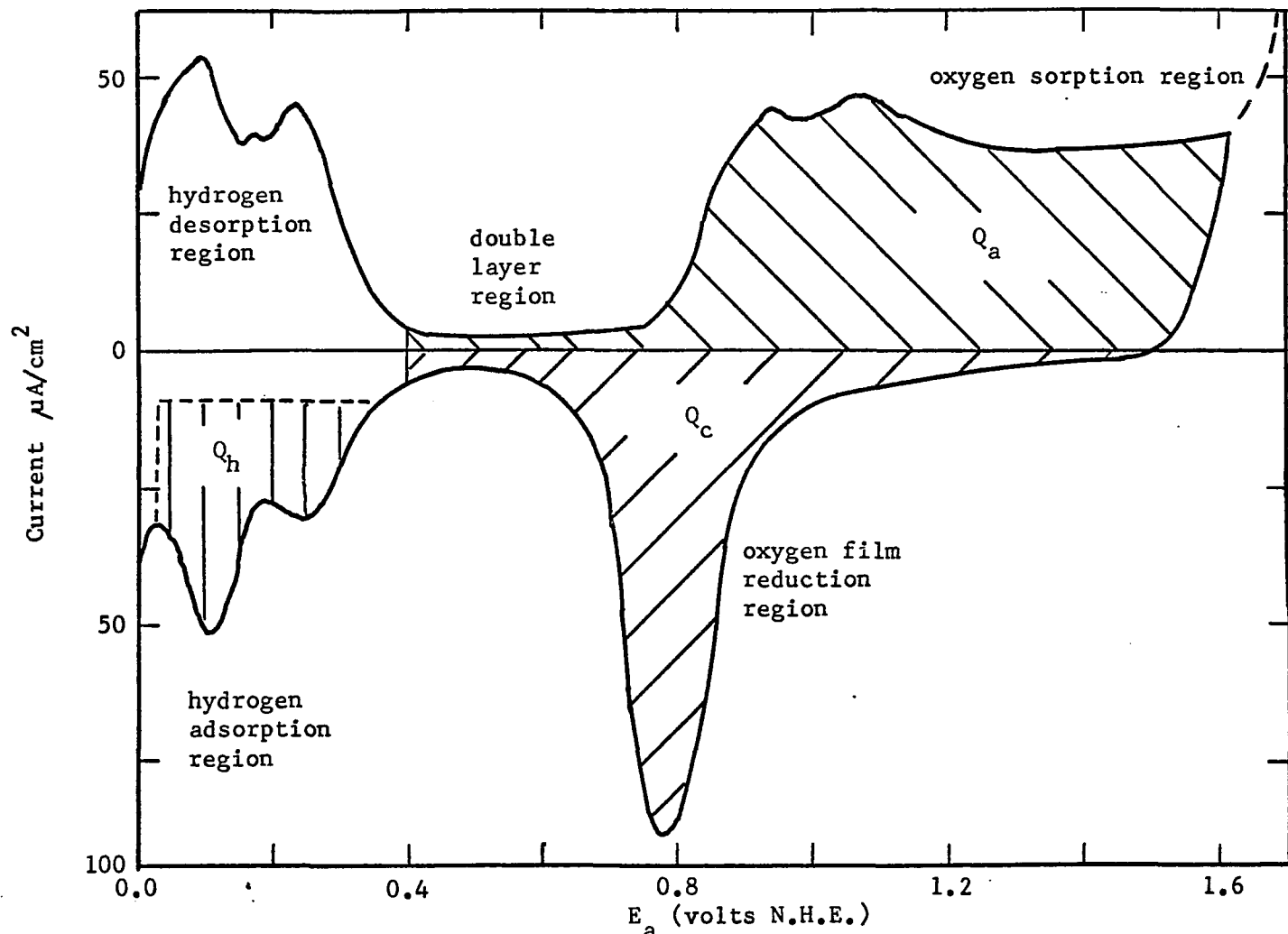


Figure 1. Typical Current-voltage Curve.

(platinum electrode in 0.5 F sulfuric acid, sweep rate 50 mV/sec)

separation is not observed. This subject is discussed in a later section.) The location of this peak varies depending on the sweep rate and on  $E_a$ , the anodic potential just prior to potential reversal. Increases in either sweep rate or  $E_a$  cause the potential of the reduction peak to move to more cathodic potentials. The potential range between 0.4 and 0.0 V is known as the hydrogen adsorption region characterized by two peaks corresponding to adsorption of hydrogen atoms. In acid solutions,  $(H^+) = 1$  molar, hydrogen gas is evolved at about 0.0 V. If an anodic transient is performed between 0.0 and 0.4 V, two peaks are observed for hydrogen desorption.

#### Activation of Platinum Electrodes

Toward many electrochemical reactions, a platinum indicator electrode shows enhanced reversible behavior if it is first activated, i.e., anodized and then cathodized (an ac treatment) just prior to use (Beans and Hammett 1925).

Several investigators have attributed this effect to the desorption of adsorbed surface-active contaminants. This desorption might be effected by disruption of the surface during formation and removal of the oxygen film or by oxidation and desorption of organic and cationic species at highly positive potentials. Of course the subsequent loss of activity would be caused by adsorption of new contaminants from the solution. This view has been expressed recently by Warner, Shuldiner, and Piersma (1967) and James (1967).

The other theories include consideration of impurity desorption but stress some additional mechanism as being of greater relative

importance. The platinization theory of Anson and King (1962) suggests that ac cycling leaves a thin layer of active platinum atoms on the surface, a light platinization, which is subsequently covered by impurity adsorption or rearranges to a more stable inactive form. The basis for this theory is the observation of surface coarsening, resembling a conventionally platinized platinum electrode, resulting from repetitive ac cycling. This coarsening has been observed recently by Biegler (1969) using electron microscopy.

Several investigators have proposed mechanisms involving special forms of surface oxygen left after the final cathodic half-cycle which have properties which cause the activation effect. The proposals of Feldberg et al. (1963) and Davis (1960) have been criticized by James (1967). The proposal of Lauer (1967) of an electro-inactive Pt(IV) oxide will be discussed later. Two separate theories based on absorption of large quantities of oxygen into the bulk platinum will also be discussed in a later section.

#### Amount and Rate of Oxygen Film Formation

Most investigators agree that the amount of oxygen film formed increases linearly between 1.0 and 1.7 V. Above this potential, Mayell and Langer (1964) observed a decrease. Fleischman, Mansfield, and Wynne-Jones (1965) observed increases and decreases, depending on conditions. Biegler and Woods (1969) observed an increase up to 2.0 V and a constant value above this potential.

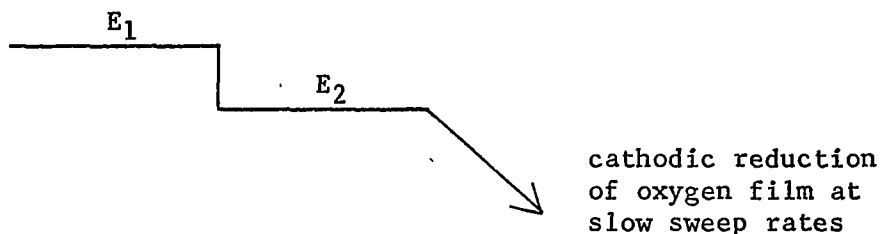
At constant potential, the rate of formation increases rapidly during the first 15-20 sec, and then the rate decreases to a value dependent upon the logarithm of anodization time thereafter (Laitinen and Enke 1960 and Gilroy and Conway 1968). Gilroy and Conway (1968, Figure 4a) observed a rapid increase in the amount of oxygen film during the first 20 sec, followed by a period of slower growth in which the amount of film increased linearly with  $\log t$ , up to 15 min, indicating that more than a single layer of Pt-O species were formed (and/or an increase in the oxidation state of the platinum) and that a "complete layer" of oxygen film was not formed at potentials up to 1.8 V. A monolayer of one oxygen atom per surface platinum atom should require between 0.4 and 0.5  $\text{mC/cm}^2$  (true surface area) of charge during reduction (Laitinen and Enke 1960 and Biegler 1969). The value of the charge corresponding to one oxygen per surface platinum atom is uncertain because the number of surface platinum atoms can only be estimated. Anodization at 1.8 V for 15 min gave 1.12  $\text{mC/cm}^2$  of cathodically reducible material. If the roughness factor of 1.5 is considered, this charge would correspond to 1.8 oxygen atoms per platinum atom with the platinum in the +2 oxidation state and all oxygen on the surface. These data of Gilroy and Conway (1968) also showed that of the oxygen film formed in 15 min, 90% was formed during the first 20 sec. Similar data were previously obtained by Laitinen and Enke (1960). They also obtained interesting data during the first 0.1 sec of constant potential anodization at potentials between 0.95 to 1.75 V. They made photographic records of the electrode current, using an oscilloscope, and found that the number of coulombs

passed was always larger (sometimes twice as large) than the amount of surface oxygen determined chronopotentiometrically after a 30 sec anodization at the same potential. Thus, in addition to formation of a stable Pt-O species, an additional reaction such as removal of impurities or formation of a transitory Pt-O species was occurring. Nevertheless, many critics have discounted the data of Laitinen and Enke (1960) as being impurity desorption. Shuldiner and Warner (1965) argued that the formation of adsorbed oxygen was complete within 0.1 sec and that other processes occurred after that time.

Data have been recently obtained by Biegler and Woods (1969) which showed a linear increase in the amount of oxygen film up to about 2.0 V and, above this potential, a limiting value of  $2.66 \pm 0.05$  oxygen atoms per surface platinum atom. The data were obtained by anodizing a platinum wire electrode for 10 sec in 1 F sulfuric acid and measuring the charge required to remove the oxygen film. The charge passed in the oxygen desorption region,  $Q_c$ , was compared with the charge passed in the hydrogen adsorption region,  $Q_h$ , and the ratio  $Q_c/2Q_h$  was equated with the number of oxygen atoms per surface platinum atom (see Figure 1). This reasoning assumes that during hydrogen adsorption, each surface platinum atom is bonded to one hydrogen atom (one electron per platinum atom). Each oxygen, which becomes bonded to a surface platinum atom, requires two electrons. The value of  $Q_c/2Q_h$  reached a limiting value of 2.47 above 2.2 V for ten seconds of anodization. By anodizing at 2.98 V, the limiting value of 2.66 oxygen atoms/platinum atom, corresponding to complete coverage, was reached within 100 sec and stayed constant up to 5,100 sec.

### Hysteresis Effects

Hysteresis effects have been observed by several investigators who formed oxygen films at an upper potential  $E_1$ , lowered the potential to a new value  $E_2$ , and then reduced the film with a cathodic transient.



Data have been obtained by Laitinen and Enke (1960), Lauer (1967), and Gilroy and Conway (1968). Data obtained by Gilroy and Conway (1968, Figure 4a) for  $E_1 = 1.5$  V for 5 sec and  $E_2 = 1.2$  V for times between 1 sec and 15 min show that the amount of oxygen film subsequently reduced is constant (independent of time at  $E_2$ ) at about 94% of the amount found without step  $E_2$ . The decrease in the amount of film occurred within one second after the start of  $E_2$ . Apparently the amount of oxygen film quickly changes to a new "thickness" which does not increase with additional time at  $E_2$ . This amount of film is about 50% larger than was observed if step  $E_1$  had not been performed. Unfortunately, Gilroy and Conway did not report hysteresis data over a wider potential range.

Previously Gilman (1964) had reported that if  $E_2$  were 1.55 V and  $E_1$  were a more anodic potential, the amount of current passed during reduction was the same as if step  $E_2$  were not performed. This implied that the reducible oxygen films formed at potentials more anodic

than 1.55 V were not altered by step  $E_2$  at 1.55 V. Recently, Biegler (1969) used a hysteresis-type sequence whenever step  $E_1$  produced oxygen evolution. After step  $E_1$ , the solution was vigorously degassed with nitrogen while the potential was held at  $E_2 = 1.28$  V.

Further data were obtained by Hoare (1966) who performed steady-state polarization measurements in oxygen-saturated 1 F sulfuric acid. During a step-wise anodic transient, he identified a region between 1.05 and 1.45 V in which the surface was progressively covered with a film of electronically conducting Pt-O. Between 1.45 and 1.80 V, oxygen evolution was observed with a large increase in current. Between 1.80 and 2.00 V, a limiting current was observed which was attributed to conversion of Pt-O sites to Pt-O<sub>2</sub> sites. At this point a step-wise cathodic transient was performed with a decrease in current observed until 1.55 V was reached. When the potential was lowered between 1.55 and 1.15 V, virtually zero current (less than one  $\mu\text{A}/\text{cm}^2$ ) was observed. Below 1.15 V the cathodic current increased because oxygen was being reduced. Hoare compared these data with those obtained using a palladium electrode under similar conditions. Palladium forms PdO which is a poorly conducting film and PdO<sub>2</sub> which can decompose to PdO and O<sub>2</sub>. When the anodized Pd electrode was reduced, an oxide reduction current was observed which corresponded to reduction of PdO<sub>2</sub> to PdO. This reduction current was not observed for the Pt electrode. Hoare concluded that Pt-O<sub>2</sub> was formed above 1.80 V which decomposed to Pt-O and O<sub>2</sub> before 1.55 V was reached because a large reduction current was not observed above 1.55 V. Below 1.5 V the surface was covered with a monolayer of

adsorbed oxygen atoms, Pt-O, which does not change between 1.50 and 1.15 V because no current flow was observed in this potential region.

It appears that these data on hysteresis behavior and their interpretations are incompatible.

#### Reduction of the Oxygen Film

As mentioned earlier the position of the oxygen film reduction peak moves negatively between 0.8 and 0.6 V with increased sweep rate or with increased anodization potential. However, the reduction peak is distorted into two components when sweep rates and anodization potential are increased above certain limits. Gilroy and Conway (1968) observed this distortion by obtaining differential galvanostatic reduction curves (the first derivatives of the chronopotentiograms) which showed two maxima when the anodic potential was above 1.6 V. The reduction current density required after the anodization at 1.6 V was not given, but data after anodization at 1.9 V for 5 sec showed two maxima when the reduction current density exceeded about  $2 \text{ mA/cm}^2$ . Under potentiostatic conditions, Will and Knorr (1960) observed reduction peak separation when cycling the electrode potential (in 4 F sulfuric acid) between 0.05 and 1.55 V at sweep rates above 5 V/sec.

The most striking evidence for separation of the reduction peak into components and for the movement of the reduction peaks to more cathodic potentials has been obtained by Ramaley and Laitinen (1966). They performed the following experiments using an oscilloscope to observe the current-voltage curve during the reduction step. The data are in Table 1.

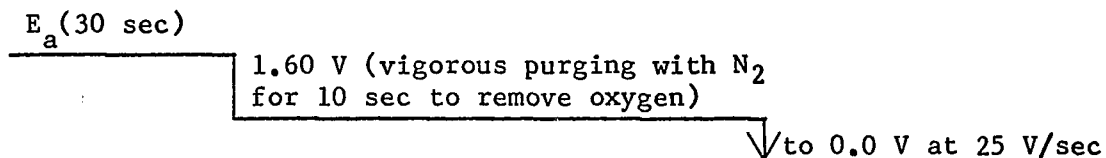


TABLE 1

## LOCATION OF REDUCTION PEAKS DURING RAPID REDUCTION

(1 F HClO <sub>4</sub> , deaerated, sweep rate 25 V/sec)				
E <sub>a</sub>	Potential of Oxygen Reduction Peaks		Size of Oxygen Reduction Peaks	Comments on Hydrogen Adsorption Peaks
Volts	E <sub>1</sub>	E <sub>2</sub>		
1.7	0.53 (0.69) <sup>a</sup>		- -	both peaks shown
1.8	0.49 (0.67)		- -	both peaks shown
1.9	0.48 (0.65)		- -	both peaks shown
2.0	0.48 (0.63)	0.38	1st peak slightly larger than 2nd peak	only one peak
2.1	0.46 (0.61)	0.31	2nd peak larger than 1st peak	only one peak
2.2	0.43 (0.60)	0.22	2nd peak much larger than 1st peak	no peaks shown

a. These potentials were obtained in 0.5 F H<sub>2</sub>SO<sub>4</sub> at a sweep rate of 50 mV/sec; see text for discussion.

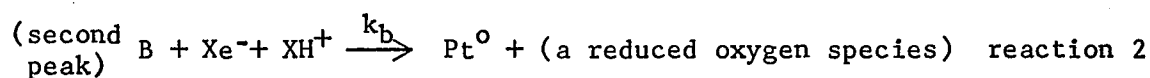
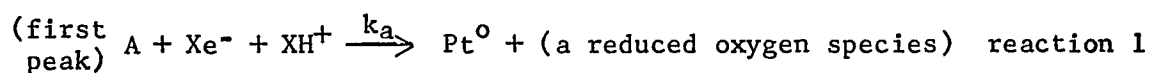


During these rapid reductions, the reduction peaks were traversed in 20 msec or less. The reduction peak separates into two components with the second (more cathodic peak) becoming relatively larger and moving into the hydrogen adsorption region obscuring the normally observed peaks. The single hydrogen peak observed after reduction with  $E_a = 2.0$  and 2.1 V was at its normal potential. After each of the reduction transients, the potential was reversed and both hydrogen desorption peaks were observed at their normal potentials. Because the hydrogen desorption peaks were undisturbed, the hydrogen adsorption reaction must have been unaffected by any oxygen remaining on the surface, or more likely all of the oxygen must have been removed. Because the hydrogen adsorption and desorption peaks were not greatly altered, the platinum surface was not greatly changed by a single cycle of anodization at high potentials and rapid reduction.

The peak potentials listed in parentheses in Table 1 were obtained at a slow sweep rate, 50 mV/sec. These reduction peak potentials were added to the data of Ramaley and Laitinen to show that the potential of the first peak is shifted a constant 150-180 mV cathodically by the faster sweep rate. This suggests that the first peak during the rapid reduction corresponds to reduction of the same species as reduced during a slow reduction. The platinum-oxygen species being

reduced in the second peak is not formed at low potentials, and it is not reduced during slow reductions in a separate peak.

These data indicate that more than one electrochemical process is occurring. There might be two types of Pt-O bonding differing in their electrochemical rate of reduction, and an equilibrium might exist between the two forms. Let the symbols A and B represent these two different types of bonding between platinum and oxygen.



Alternative mechanisms may be devised which include unlikely steps. The proposed mechanism is the simplest, but not necessarily the only one, which agrees with the experimental observations. (The use of "X" in the above equations is not intended to mean that the corresponding numbers are necessarily equal or integers. They merely represent the values required to balance the reaction if all reactants and products were known and specified.) The reduction of species A (reaction 1) would correspond to the reduction peak normally observed during slow sweep rate reductions or to the first peak during a fast sweep rate reduction when reduction peak separation is observed. The reduction of species B (reaction 2) would occur in the same potential range as for species A (reaction 1) during slow sweep rate reductions. During fast sweep rate reductions, species B (reaction 2) is reduced in a separate, more cathodic peak.

A proposed mechanism for the removal of the oxygen film must be compatible with the mechanism of the formation of the film. For example, if a proposed film formation mechanism places a large fraction of oxygen beneath the surface, a compatible film reduction mechanism must show how this oxygen becomes reduced. It is concluded that sufficient information is not available to adequately describe either process. For this reason, the general symbols A and B were used in preference to notations such as "PtOH" or "PtO".

Gilroy and Conway (1968) have considered data obtained by several techniques (and several other investigators) and data for platinum and other noble metals. They have concluded that: "A completely irreversible transformation from a Pt"OH" or Pt"O" dipolar ad-layer to a two-dimensional oxide (Pt O Pt O . . . in the ad-layer) in domains seems to be the type of explanation required."

#### Existence of a Weakly Adsorbed Platinum-Oxygen Species

A weakly adsorbed platinum-oxygen species would be an oxygen-containing species weakly bonded or adsorbed on the platinum surface. Formation of this species would involve oxidation of either a platinum atom on the electrode surface or oxidation of a water molecule on the electrode surface. There are numerous oxygen-containing oxidative decomposition products of water, and only a very small amount of this species might be formed. The identification of this species will probably be made after its existence is proved and its characteristics are determined.

The work of Shibata (1964) showed some evidence for the existence of a weakly adsorbed species. As mentioned previously, the charge,  $Q_a$ , required to form the film is larger than the charge,  $Q_c$ , required to remove the film (see Figure 1). Shibata observed that the ratio  $Q_a/Q_c$  was constant when  $E_a$  (during ac transients) was above 1.2 V, but the ratio increased when  $E_a$  was below this potential. This increase in the ratio was larger when the electrode was left at open circuit for two minutes between steps  $Q_a$  and  $Q_c$ . The ratio increased even more if the solution was agitated during the two-minute waiting period. In further experiments, the solution was agitated during the anodization step (but not during the cathodization step). When  $E_a$  was below 1.05 V,  $Q_c$  was essentially zero. The species formed during the anodization step was removed by the agitation of the solution and was not on the electrode surface when step  $Q_c$  was performed. Under these conditions of vigorous agitation during step  $Q_a$ , a constant ratio of  $Q_a/Q_c$  was not observed until  $E_a$  was increased to above 1.3 V. The constant values attained for the ratio of  $Q_a/Q_c$  were 1.3 for the stationary solutions and 1.8 for the agitated solutions. Supporting evidence of electrode capacity data was also obtained. These data might be criticized as being caused by reaction with solution impurities, but the amounts of charge involved appear to be too large.

Further data obtained by other investigators studying  $Q_a/Q_c$  ratios under various experimental conditions may also apply. In a study by Breiter (1966), the values of  $Q_a$  and  $Q_c$  approached each other after 110 cycles between 0.2 to 1.5 V. As pointed out by Biegler

(1969), the difference between  $Q_a$  and  $Q_c$  did not disappear, and the total difference after the 110 cycles was  $40 \text{ mC/cm}^2$  which seems too large to attribute to impurity adsorption. In his own work, Biegler (1969) observed that the shape of the current-voltage curves (ac cycling between 0.05 and 1.54 V) changed during the first 200 cycles but did not change thereafter up to 500 cycles. A constant difference between  $Q_a$  and  $Q_c$  was observed. It appears that in the first stage of ac cycling, impurity desorption and rearrangement of the surface platinum atoms were responsible for the changes observed in the current-voltage curves. During the last stage of this ac cycling, the observed difference between  $Q_a$  and  $Q_c$  was probably too large to be attributed to these causes.

#### Activations Resulting From Long-Term Anodization Procedures

Shibata (1963) performed a series of complicated and lengthy anodic pretreatments on his electrodes. He then measured the resulting electrode activity and its subsequent disappearance. The most striking result of this work was that, although all pretreatments gave the same initial high activity, the stability of the electrode activity was better when the pretreatments were severe and lengthy. Another feature of the work of Shibata, later extended by Kozawa (1964), was a large reduction peak in the hydrogen adsorption region, at 0.2 V, which appeared only during reduction of severely anodized platinum electrodes. This low potential reduction peak was attributed to a "thick oxide layer" corresponding to 40 oxygen atoms for each surface platinum atom.

The surface, after reduction of this thick oxide layer, possessed a stable high activity which Shibata attributed to strain remaining in the surface layers of platinum atoms.

Hoare (1963, 1965) immersed platinum electrodes in concentrated nitric acid for more than 50 hours forming an electrode surface of very stable high activity. Chemical analyses of the electrodes showed an increase in the oxygen content of the surface layers (Hoare, Meibuhr, and Thacker 1966). Treated and untreated electrodes were analyzed for oxygen content by a vacuum fusion technique which showed the slight increase in oxygen content. X-ray diffraction studies showed shifting of lines, but no new lines, indicating that oxygen had penetrated the platinum lattice producing an alloy but not a new phase oxide.

The activity of these electrodes was caused by oxygen in the surface layers and not the oxygen on the surface. These electrodes with the large amount of subsurface oxygen were described by Hoare as a new material, a Pt-O alloy. The stability of the Pt-O alloy was exceptional.

The works of Shibata and Hoare described in the preceding paragraphs indicate that they have formed electrodes which are significantly different from those usually prepared by brief activation schemes. Their electrodes retained a high activity under conditions which have promptly deactivated electrodes given only brief or even repetitive ac treatments. It has been concluded by these investigators and by James (1967) that brief anodization or ac treatment schemes are useful in cleaning the electrode surface and forming an activated

surface. This activation will be lost comparatively quickly by adsorption of solution impurities. These extended pretreatments have the advantage of forming active surfaces that are qualitatively different and exceptionally stable in comparison with those formed by brief anodization schemes.

### Summary

The oxygen films on platinum electrodes are not simple but rather complex in their effect upon platinum as an inert material for indicator electrodes and for other uses. It must be emphasized that the oxygen films are electron-conducting and good conductors of electricity, as contrasted with the oxygen films for some other metals which are ion-conducting and poor conductors of electricity.

It has been established that pretreatment of platinum electrodes must be considered before they can be used for any given application. It has also been established that electrode performance in some instances can be improved by an "activation procedure." The means by which this activation is accomplished is still the subject of controversy. The role of oxygen in forming the activated surface seems to be crucial. Whether the oxygen is (a) on the surface, (b) in the first few layers below the surface, or (c) just recently removed from the platinum has not been determined to everyone's satisfaction. There is agreement that all procedures for activating a surface will cause desorption of impurities, and that loss of activity is caused by or is accompanied by readsorption of impurities.



The kinetics of film formation, film removal, and changes during hysteretic treatments have not been fully investigated under all conditions. The available data do not indicate that a simple description of a homogeneous monolayer is an adequate model. On the contrary, the existence of more than one kind of platinum-oxygen bonding seems essential to reconcile the existing data. Whether this bonding can be described as simple Pt(II) and Pt(IV) oxides is not certain because the electrochemical data on film formation, film removal, etc., have not been correlated with easily defined chemical oxidation states. Finally, the effects of breaking these platinum-oxygen bonds upon the resulting metal surface is not known.

Through the previous data discussion, it is apparent that basic changes in the oxygen film occur depending on the anodization potential. Several investigators have shown that the oxygen film formed above approximately 1.60 V is different from that formed at lower potentials, although the evidence in some cases was of questionable validity. Two examples are: a slight change in the slope of a curve for amount of reducible material versus anodization potential and changes in the rest potential of an electrode with anodization potential.

The separation of the reduction peak during rapid reductions is unmistakable evidence that the oxygen film formed above 1.60 V is different from that formed at lower potentials. The early work of Will and Knorr (1960) showed that rapid reduction could reveal information that was not observed during slow reductions. The data obtained by Ramaley and Laitinen (1966) showed that the effect observed by Will and

Knorr depended on anodization potential. The movement of the more cathodic reduction peak into the hydrogen absorption region was clear evidence that electrochemically different platinum-oxygen bonds were being formed.

The data obtained by Anson and Lingane (1957) using chemical removal of the oxygen film showed that Pt(II) and Pt(IV) oxides were present in a 6 to 1 molar ratio. However, the anodization conditions employed were below 1.60 V, revealing nothing concerning the oxygen films formed at higher potentials. It was decided to investigate the oxygen films formed at higher potentials using chemical removal of the film to determine the ratio of Pt(II) to Pt(IV) and the total amount of removable film.

### Research Goals

The main goal of this research was to investigate the properties of oxygen films formed over the widest possible potential range. The molar ratio of Pt(II)/Pt(IV) and the amount of oxygen film was to be determined by chemical dissolution of these films. Of special interest were those films formed at anodization potentials above 1.60 V. To accomplish this goal it was necessary to establish additional goals which are listed below.

1. Determine the amount of oxygen film, formed over the widest possible potential range, using a cathodic reduction transient to measure the amount of film.

2. Correlate the amount of charge required to electrochemically remove the oxygen film with the amount of charge corresponding

to the sum of the two platinum ions observed from the chemical dissolution of the oxygen film.

3. Determine the lowest anodization potential at which oxygen films are formed that can be detected by the two methods of removing the films.

4. Determine the amount and molar ratio of Pt(II)/Pt(IV) of any oxygen film remaining on the electrode surface after either exposure to hot hydrochloric acid or after a cathodic reduction transient.

5. Determine the experimental conditions under which detectable amounts of oxygen film are not removed from an anodized platinum electrode by these two film removal procedures.

The goals of items 1 through 3 were established to compare the total amount of oxygen film removed by the two different procedures. A reasonable agreement between the two sets of data would be evidence that both procedures were giving reliable data. The goals of items 4 and 5 were established to develop methods of obtaining information to meet the goals of the preceding items.

The principal method of obtaining information during this research was by chemical dissolution of oxygen films. Because this method is not universally accepted, it was an inherent part of this study to evaluate this method of obtaining information. This was to be done by evaluating the data obtained to meet the goals described above and by a critical review of previously published information.

## EXPERIMENTAL APPARATUS AND PROCEDURES

### Preparation of Solutions

Because control of impurities in the solutions was essential, distilled water from the chemistry building central supply was purified by slurring it with activated charcoal ("Darco" G-60, Matheson, Coleman and Bell, East Rutherford, N. J.) and filtering to remove the charcoal. The filtrate was distilled from an alkaline solution in an all-Pyrex system. To minimize any possible contamination problems, the purified distilled water was stored in well-aged glass bottles and was not prepared in quantities larger than required for a few days.

Sulfuric acid, 0.5 F, was prepared by diluting reagent grade concentrated acid with the purified distilled water described above. Again only sufficient acid was prepared for a few days. The electrolysis steps were performed with this 0.5 F sulfuric acid. An attempt was made to further purify the dilute sulfuric acid by slurring it with purified activated charcoal. The charcoal was leached four times with 8 F HCl (constant boiling) for 12 hours just below the boiling point. Three hot, 12-hour leaches with purified distilled water were performed, and the filtrate gave no visible color when tested for ferric ions with orthophenanthroline. Portions of 0.5 F sulfuric acid were slurried with this activated charcoal and filtered (a test for chloride with silver ion was negative). Current-voltage curves obtained with these purified solutions were compared with those from untreated solutions. The currents passed between 0.4 and 1.4 V at 0.05 cps were

compared, showing that with the treated solutions about 5-10% less current was passed with no noticeable difference in the shape of the curves. When the purified activated charcoal was added directly to the electrolysis cell, the current between 0.4 and 1.4 V increased by over 50%, and the current was found to increase slightly with increase in agitation. Before the charcoal was added, the current did not change when agitation was varied. The use of the purified activated charcoal was discontinued.

Hydrochloric acid, 1 F, used to remove the oxygen films from the anodized electrodes, was prepared from constant boiling hydrochloric acid and the purified distilled water. The constant boiling hydrochloric acid was prepared by mixing equal volumes of reagent grade hydrochloric acid with purified distilled water, distilling this mixture, and collecting the middle half of the distillate.

#### Electrolysis Cell

The electrolysis cell was a modified 250-ml Pyrex beaker with gas inlets at the solution level and at the bottom. The gas inlet at the bottom of the cell had a fine porosity glass frit. At the side of the cell, a ground glass fitting was provided for the bridge to the reference electrode. The bridge was drawn to a fine tip which just touched the indicator electrode. The other end of the bridge, which had a medium porosity glass frit, was placed in a 150-ml beaker into which was also placed a saturated calomel reference electrode. The electrolysis cell, the bridge, and the 150-ml beaker all contained the same solution, 0.5 F sulfuric acid. A drain was provided for the

electrolysis cell so that the electrolysis solution could be changed before each use (see Figure 2).

The top of the cell was a teflon plate (9 x 9 x 0.5 cm) with a groove to permit a tight fit when placed on the electrolysis cell. In the center of the teflon plate a 1.6-cm hole held the indicator electrode in a reproducible position. Two counter electrodes were permanently placed on opposite sides of the cell. A funnel, which entered the cell through the cover, was used for filling the cell and as a gas exit.

Nitrogen gas for removing oxygen from the sulfuric acid solutions was purified by passing it over hot copper turnings. All of the stopcocks in the system were lubricated with concentrated sulfuric acid to avoid using any stopcock greases which might have led to contamination problems. Purging the solutions with nitrogen through the glass frit at the bottom of the cell required at least 15 min. The presence of residual oxygen could be observed by recording current-voltage curves between 0.4 and 1.4 V. A cathodic current between 0.4 and 0.6 V during an anodic sweep was considered proof that oxygen remained. A slow nitrogen flow was maintained during all electrolyses. No provision was made for temperature control, and all electrolyses were made at  $25 \pm 2^\circ$ .

#### Platinum Electrodes

The indicator and the two counter electrodes were made of platinum foil, 1.50 x 4.75 cm (14.25 cm<sup>2</sup> considering both sides), attached to platinum wires sealed in soft glass tubing. The platinum wires were

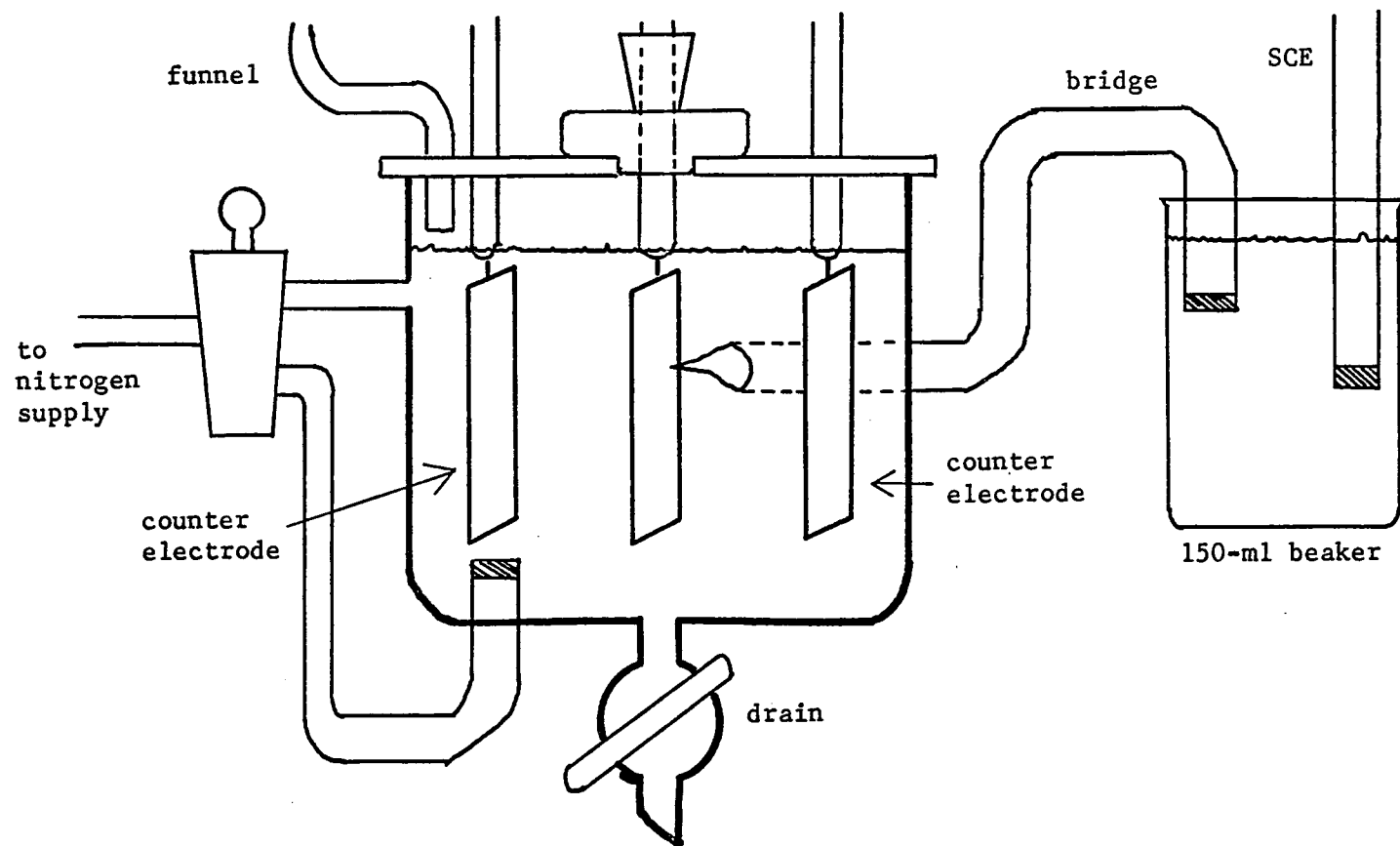


Figure 2. Electrolysis Cell.

silver-soldered to copper wires which extended up and out of the glass tubing.

The two counter electrodes were permanently clamped into position and not moved during the study. The indicator electrode glass tubing was placed in a thermometer adapter (Kontes K-179800). A circular teflon plug with a center hole for the indicator electrode was machined to provide a tight fit for the thermometer adapter. On the lower part of this plug, the teflon was removed, exposing a 1.6-cm circular rim which fitted snugly into the center hole in the cell cover. It was possible to position the indicator electrode reproducibly between the counter electrodes and to remove it from the electrolysis cell quickly without breaking any electrical connections. The adapter and plug which positioned the indicator electrode in the electrolysis cell cover also fitted the dissolution tube which will be described later.

The two counter electrodes obviously connected to each other were placed on both sides of the indicator electrode 2.85 cm away. This cell configuration exposed both sides of the indicator electrode to an equal current density. The  $iR$  drops from each counter electrode to the indicator electrode were the same. This arrangement was chosen because it was desired to form oxygen films on both sides of the electrode under conditions of minimum potential and current density gradients over the electrode surfaces. Of the many geometric arrangements that were considered, the one chosen seemed to be the simplest that



would meet these requirements. An excellent review of the problems was considered by Harrar and Shain (1966).

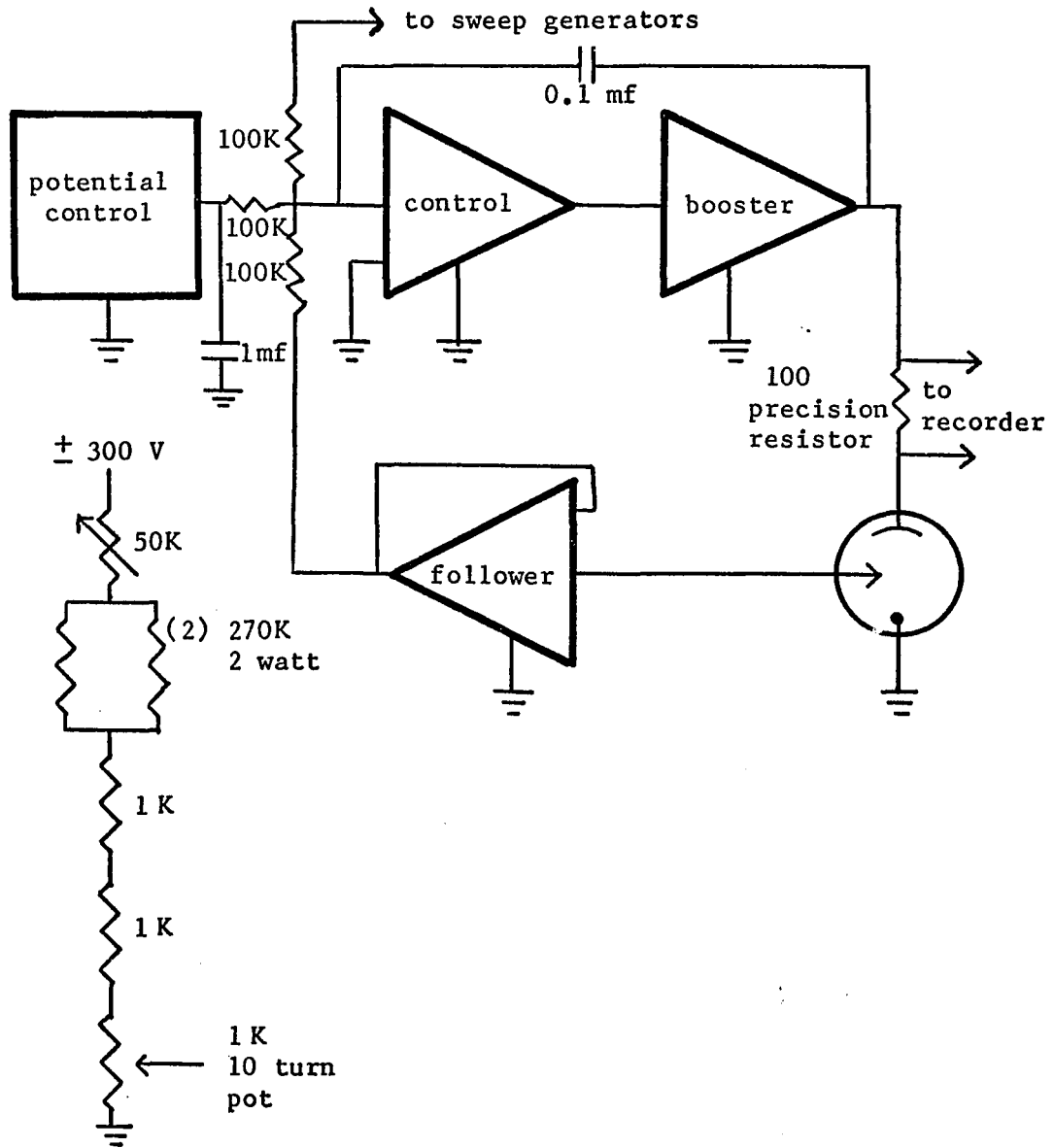
The distance separating the indicator and counter electrodes was not shown by preliminary experiments to be a critical factor. The separation chosen permitted using a cell of convenient size. Gaseous products produced at the electrodes probably were not transported to the other electrodes within the electrolysis times used. The electrodes were placed vertically not only for convenience but, more important, so that gaseous products would not collect upon the electrode surfaces and possibly distort the current density or potential across the face of the electrodes.

The size of the electrodes was chosen as a compromise between several factors. The largest possible surface area was desired to maximize the amount of oxygen film formed. However, at the conclusion of the dissolution step, the maximum concentration of platinum ions was desired for spectrophotometric measurements. Thus, a minimum of acidic stripping solution was desired. With the requirement that the acidic stripping solution be deaerated, a tube of circular or elliptical cross section permitted the smallest possible solution volume. The availability of spectrophotometer cells of 10-cm path length containing only 5 ml of solution made it possible to use 10-ml volumetric flasks to hold the stripping solutions after the chemical dissolution of the film. Thus, the size of the dissolution tube, described later, determined the electrode shape and size.

### Instrumentation

Figure 3 is a diagram of the potentiostat used to maintain a constant potential between the indicator electrode and the reference electrode. The potentiostat was capable of delivering 1 amp at  $\pm 150$  V (for delivering large currents through high resistances.) Although the cell resistance was quite low (1 F acid), the additional current capacity was desired because the electrodes to be used were large ( $14.25 \text{ cm}^2$ ). The control amplifier was a G. A. Philbrick Researches Model UPA-3, and the follower was a GAPR Model SK2-V stabilized by an SK2-P. The booster amplifier was a simple cathode follower built using eight 6AS7 power tubes in parallel with four 75W standard incandescent light bulbs in parallel as cathode resistors. A GAPR R-100 power supply was used for the GAPR amplifiers. The booster amplifier was powered by a nonregulated, well filtered, full wave bridge,  $\pm 250$  V power supply.

The triangular potential sweeps used for electrode pretreatment were generated by a Wavetek Model 104 General Purpose VCG sweep generator. The current-voltage curves for electrode area measurements were recorded with a Sargent Model MR recorder. The triangular sweep generator for generating the sweeps for measuring the cathodically reducible material was custom built with provision to sweep between adjustable potential limits at a variable sweep rate. The current-voltage curves in this part of the study were recorded using a Moseley Model 2D-2A X-Y recorder.



Detail of potential control (two provided)

Figure 3. Potentiostat.

Procedure for Forming Oxygen Films -  
Length of Anodization Time

The length of the anodization time was chosen at 30 sec as a compromise between several factors. It was desired to form the maximum amount of oxygen film so that the absorbance of the hydrochloric acid solutions would be as high as possible. The data of Laitinen and Enke (1960) and Gilroy and Conway (1968) showed that 90% of the cathodically reducible material was formed in the first 30 sec at potentials up to 1.8 V. These data indicated that most of the platinum-oxygen bonds were formed within the first 30 sec. After this time the amount of cathodically reducible material increased with  $\log t$  for anodization times up to 900 sec at 1.8 V. During the period when growth was proportioned to  $\log t$ , rearrangement could have been occurring which would have altered the initial bonding. It was decided that information on the initially formed platinum-oxygen bonds was preferred, and that these data could be compared later with data at much longer anodization times. The data of Laitinen and Enke (1960) and Gilroy and Conway (1968) showed that the cathodically reducible material increased quite rapidly during the first 15 sec of anodization. However, data were available only up to 1.8 V and the initial rapid growth period could have required a longer time above this potential. Also it was desired to manually remove the electrode from the electrolysis solution with the potential still applied. This would prevent any possible loss of oxygen film if the anodization potential were stopped and the electrode allowed to remain in contact with the sulfuric acid (and electrolysis products) for even a few seconds. With the relatively long 30-sec

anodization time, any error caused by manual removal of the electrode was minimized.

After the present study was completed, Biegler and Woods (1969) published data showing the cathodically reducible material formed during 10 sec of anodization at potentials up to 2.98 V. At all potentials, they reported that the cathodically reducible material values were not quite constant for 10 sec of anodization, but at 2.98 V a limiting value was obtained when the anodization time was extended between 100 to 5100 sec. Although the data reported are scanty, the period when the growth rate is proportional to  $\log t$  apparently becomes shorter and perhaps disappears in the potential range between 1.8 and 3.0 V.

#### Oxygen Film Dissolution Apparatus and Procedure

The procedure for dissolving the oxygen films was basically that of Anson and Lingane (1957) and Peters and Lingane (1962). In the latter paper, the anodized electrode was removed from the electrolysis cell and washed free of electrolyte with water. The electrode was placed in a clean cell, nitrogen flow was started, and deaerated 1 F hydrochloric acid was added. Deaeration was performed for an additional 10 min. The solution was heated to boiling during the course of 60 min while a rapid flow of nitrogen was maintained. After cooling, the solution was transferred to a volumetric flask and adjusted to volume with 1 F hydrochloric acid.

This procedure was modified only slightly for the present study. Because the oxygen films were formed at more anodic potentials than in the two papers listed above, it was desired to minimize any possible loss of oxidized platinum atoms through self-discharge or other mechanisms. The 1 F hydrochloric acid (about 9 ml) was placed in the dissolution tube and deaerated for at least 10 min with a rapid stream of nitrogen. The washed anodized electrode was inserted into the dissolution tube and kept above the acidic stripping solution level while the rapid nitrogen flow was continued. Solution deaeration was hastened by the size and shape of the dissolution tube. This tube was 1.6 cm in diameter with a medium porosity glass frit at the bottom. The height was 18 cm with 13 cm above the solution level. Two min after the end of the electrolysis, the electrode was lowered into the hydrochloric acid, and the dissolution tube placed in a hot water bath at 85°. The temperature in the dissolution tube reached 75° within 2 min. Thus, the oxygen film was exposed to the acidic stripping solution within 2 min and stripping at high temperature was started within an additional 2-3 min. During the 60-min dissolution step, the water bath temperature was raised to about the boiling point. The nitrogen flow rate was reduced to minimize loss of the stripping solution. After removing the apparatus from the water bath and removal of the electrode, the walls of the tube were rinsed with the stripping solution and allowed to drain for a few minutes. The solution was transferred to a 10-ml volumetric flask, allowed to cool, and the volume adjusted with 1F hydrochloric acid.

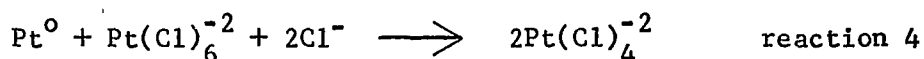
The nitrogen was filtered through activated charcoal and glass wool to remove contaminants such as grease which might absorb in the ultraviolet spectra. The nitrogen was passed through two presaturators before entering the dissolution tube. The first contained 200 ml and the second 50 ml of 1 F hydrochloric acid. The first was changed weekly and the second before each dissolution. The necessity of pre-saturation will be discussed later.

#### Procedure for Platinum Analysis

The procedure has been described in Anson and Lingane (1957) and Peters and Lingane (1962). Briefly the procedure was measuring the absorbance at 230 nm and 262 nm (the wavelengths at which Pt(II) and Pt(IV) chloro-complexes absorb, respectively). The absorbance of Pt(II) at 262 nm is negligible. In these previous studies the amounts of Pt(IV) were much smaller than the amounts of Pt(II) so that a correction for Pt(IV) absorbance at 230 nm was not performed. Measurements were made in 10-cm silica cells with pure 1 F hydrochloric acid for the comparison solution.

Two corrections were applied by Peters and Lingane: (a) an extraneous absorption was observed between 220 and 240 nm and (b) at the platinum concentrations encountered, platinum metal reduced some of the Pt(IV) to Pt(II). The extraneous absorption "blank" correction was determined by performing the stripping operation, except for anodizing the electrodes, and measuring the resultant absorbance against unheated 1 F hydrochloric acid. The amount of Pt(IV) which is converted into Pt(II) during the stripping operation was determined by heating

solutions of Pt(II) and Pt(IV) and determining the changes in their concentrations. The correction was applied by increasing the observed Pt(IV) concentration by 18% and subtracting the appropriate amount from the observed Pt(II) concentration. The known stoichiometry of the reaction shows that two moles of Pt(II) are formed from each mole of Pt(IV) reduced.



For the present study, several minor changes were made in the procedure described above. The amounts of Pt(IV) were higher in the present study, making a correction for Pt(IV) absorbance at 230 nm necessary. The equations used for calculating the concentrations of Pt(II) and Pt(IV) were as follows:

$$\text{Pt(II) in m/l} = \frac{(2.46 \times 10^4)(A_{230}) - (3.54 \times 10^3)(A_{262})}{1.93 \times 10^9} \quad \text{equation 1}$$

$$\text{Pt(IV) in m/l} = \frac{(7.86 \times 10^3)(A_{262}) - (4.07 \times 10^2)(A_{230})}{1.93 \times 10^9} \quad \text{equation 2}$$

$$\begin{aligned} \text{for Pt(II)} \quad \epsilon_{230} &= 7.86 \times 10^3 \\ \epsilon_{262} &= 4.07 \times 10^2 \end{aligned}$$

$$\begin{aligned} \text{for Pt(IV)} \quad \epsilon_{230} &= 3.54 \times 10^3 \\ \epsilon_{262} &= 2.46 \times 10^4 \end{aligned}$$

The above values for the molar absorptivity were obtained by preparing standard solutions of both platinum ions in 1 F HCl and obtaining their UV spectra.



The extraneous absorbance was also observed with somewhat greater absorbance at longer wavelengths than observed by Peters and Lingane (1962). A blank was measured at least once for each batch of hydrochloric acid prepared. The values obtained averaged 0.020 A at 230 nm and 0.030 A at 262 nm. Figure 4 shows typical UV spectra obtained during the present study.

A few experiments were performed to confirm the disproportionation data obtained by Peters and Lingane. Solutions of Pt(II), Pt(IV), and mixtures of the two were heated between 85-90° in deaerated 1 F hydrochloric acid. The concentrations of the platinum ions were between 1 and  $3 \times 10^{-6}$  F. Before these experiments were performed the platinum electrode was heated in 1 F hydrochloric acid at 85° for three hours.

Initially it was learned that platinum solutions in this concentration range, from 1 to  $3 \times 10^{-6}$  F, increased in absorbance at both 230 nm and 262 nm upon standing at room temperature for more than about three hours. Reproducible dilutions from more concentrated stock solutions (about  $5 \times 10^{-4}$  F) were prepared just prior to each experiment.

Solutions containing only Pt(II) showed little gain in absorbance at either 230 nm or 262 nm when heated for one hour with or without the platinum electrode. Solutions containing only Pt(IV) showed only very small changes in absorbance at 262 nm [where Pt(IV) absorbs] but larger and variable increases in absorbance at 230 nm [where Pt(II) absorbs]. These increases were smaller with freshly prepared Pt(IV) solutions, and the absorbance increases at 230 nm tended to become

Figure 4. Typical Ultraviolet Absorption Spectra of Hydrochloric Acid Stripping Solutions.

(1) Oxygen film formed at 2.35 V

$$\begin{aligned}\text{Pt(II)} &= 4.45 \times 10^{-6} \text{ F} \\ \text{Pt(IV)} &= 1.70 \times 10^{-6} \text{ F}\end{aligned}$$

(2) Oxygen film formed at 1.00 V

$$\begin{aligned}\text{Pt(II)} &= < 3.5 \times 10^{-7} \text{ F} \\ \text{Pt(IV)} &= < 1.2 \times 10^{-7} \text{ F}\end{aligned}$$

(3) Blank

(4) Instrument baseline

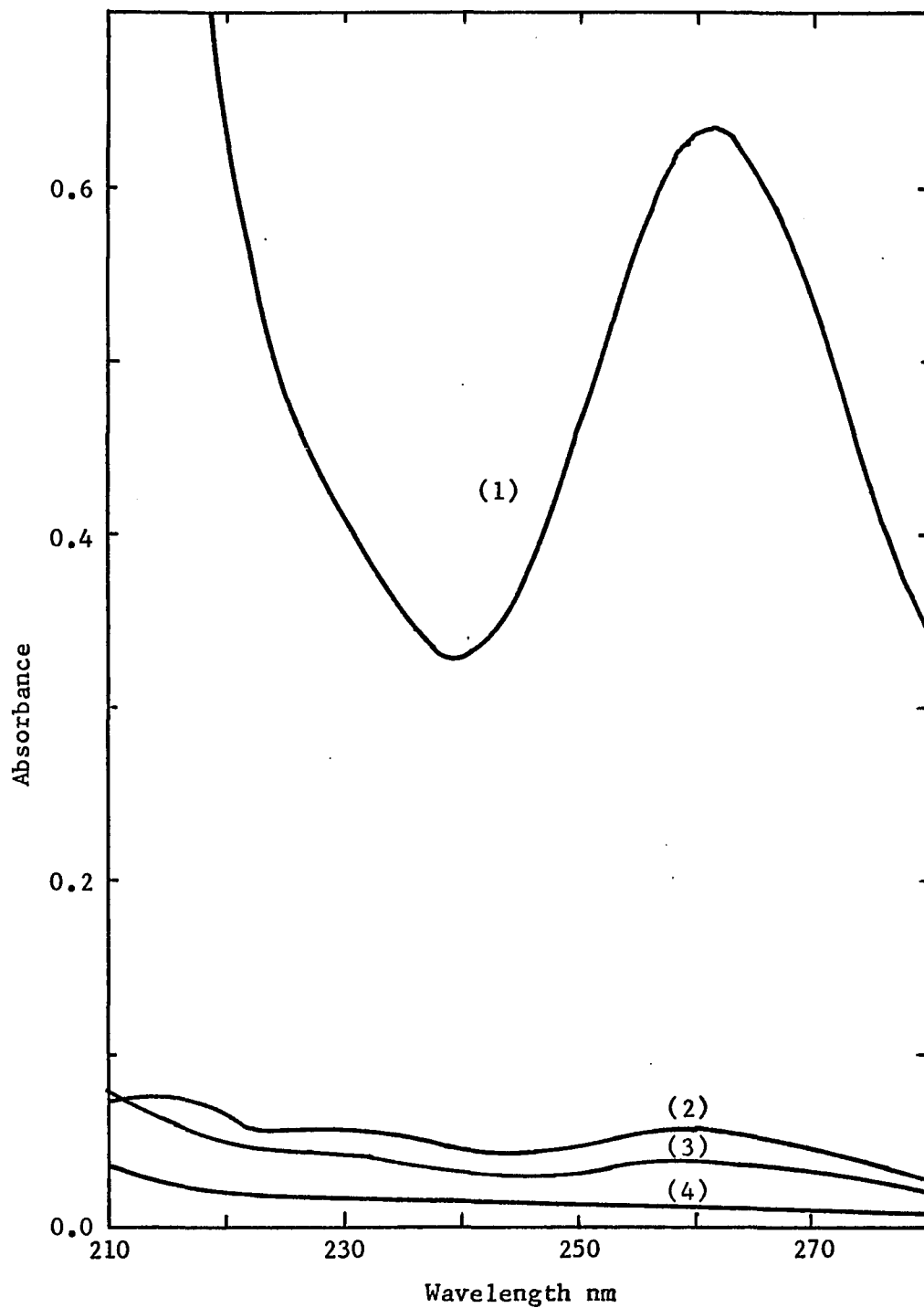


Figure 4. Typical Ultraviolet Absorption Spectra of Hydrochloric Acid Stripping Solutions.

larger when Pt(IV) solutions were more than a few hours old. (These absorbance increases were up to three times larger than the blank correction which, of course, was applied to all values.) Two solutions containing both Pt(II) and Pt(IV) were heated with the platinum electrode and gave conflicting results. The first solution lost in Pt(IV) concentration by 13% while actually showing a slight loss in Pt(II). The second solution lost 11% in Pt(IV) concentration while the Pt(II) concentration increased by slightly more than the expected stoichiometric amount.

It should be emphasized that data from previous investigators were obtained in "gently boiling" acid while the data in the present study were obtained between 85-95° which duplicated the conditions of the chemical dissolution procedure. The absorbance changes in these solutions appear to be more complex than originally believed. Rather than continuing the study of these changes by employing more elaborate equipment for temperature control, etc., it was decided to report the data without a correction because the basic conclusions from the data were not affected as explained later.

Two additional observations were made during the present study. When the acid solutions were remeasured the day after the chemical dissolution operation, the absorbances usually had increased, especially at 262 nm. However, because no effect was shown during the first three hours, it was concluded that valid data could be obtained if the spectrophotometric measurements were made within that time. Also observed were increases in absorbance at 230 nm when the acidity was above 1 F.

To maintain a constant acidity in the dissolution tube, two presaturators were included in the chemical dissolution apparatus.

The spectrophotometric measurements were made using 10-cm silica cells and a Cary Model 14 spectrophotometer was used to obtain the UV spectrum between 210 and 280 nm. Inspection of the spectra occasionally revealed an unusually high absorbance between 210 and 230 nm. These data were discarded, and the cause of these abnormal samples was not discovered.

#### Pretreatment of Electrodes

Previous investigators have stressed the importance of electrode pretreatment in obtaining valid data. Several different types of pretreatments have been used primarily because the investigator found that they were required to obtain reproducible data for his experiments. Several different types of pretreatments will now be discussed and the reasons will be given for adopting the method which was used in the present study.

Peters and Lingane (1962) placed their electrode in boiling 1 F hydrochloric acid for two to three hours. The electrode was then placed in fresh, deaerated hydrochloric acid and reduced by short-circuiting it to a large (20 cm<sup>2</sup>) saturated calomel electrode. After this pretreatment, anodic chronopotentiograms were recorded and the charge passed increased for reduction times up to 15 minutes but remained constant upon longer reduction times. It is clear that similar pretreatments will reduce or remove any oxygen film on the surface and will allow time for any slow processes to occur (such as diffusion of

oxygen from sublayers to the surface). These pretreatments do not remove many surface contaminants, and the state of the resulting surface may not be reproducible.

Other investigators have employed ac treatments to remove impurities, to reduce any oxygen film, and to leave the surface in a reproducible state. A typical example of a potential-step pretreatment (Gilman 1967, p. 127) involves three successive steps: (1) 1.8 V for 2 sec to oxidize and desorb surface impurities, (2) 1.2 V for 120 sec to maintain an oxygen film while permitting desorbed species to diffuse away from the surface, and (3) 0.4 V for 10 sec to reduce the oxygen film. This procedure would be expected to remove many surface contaminants and leave the surface in a freshly reduced state.

The two pretreatments described above are essentially different in their action. Whereas the first was probably effective in removing even the most stubborn traces of oxygen film and perhaps cationic contaminants, the second pretreatment would be relatively ineffective in accomplishing these purposes. The second pretreatment did form a freshly reduced "clean" surface, while the first would lead to a surface with little or no oxygen film but perhaps highly contaminated.

Breiter (1966) used repetitive ac cycles between 0.2 and 1.5 V at 30 mV/sec in helium-stirred 0.5 F sulfuric acid. Changes in the current-voltage curves were interpreted as showing the formation of an "activated surface." During the first 110 cycles, the changes observed were as follows: (a) in the hydrogen adsorption region, the peaks became more clearly defined and the current increased; (b) in the oxygen

adsorption region during anodic transients, the current increased between 0.8 and 1.2 V and decreased above 1.2 V; and (c) during the oxygen film reduction, the current peak became higher with more current passed. Also, a decrease in current was observed between 0.35 and 0.65 V during the cathodic transient. These changes in the current-voltage curves were associated with activation of the electrode surface.

The electrode pretreatment chosen for the present study was designed to take advantage of the desirable effects of repetitive ac cycling as described by Breiter (1966). (Hereafter in this dissertation, the term "standard pretreatment" will mean the procedure in the seven steps listed below.)

1. The electrode had invariably just been in hot 1 F hydrochloric acid for one hour in the previous experiment. The electrode was washed with purified distilled water and placed in the electrolysis cell which contained 0.5 F sulfuric acid. The sulfuric acid was drained from the cell and the cell filled with purified distilled water. Exposure to both solutions was about 5 min each. The distilled water was replaced with 0.5 F sulfuric acid.

2. A 15-min purging with nitrogen to remove oxygen was performed with the electrode at open-circuit.

3. Triangular sweeps between 0.4 and 1.4 V were performed at 800 mV/sec for 5 min (about 120 cycles total).

4. Triangular sweeps between 0.01 and 1.01 V were performed at 800 mV/sec for 5 min (about 120 cycles total).

5. Step 4 was continued for 2 to 4 min at 80 mV/sec and a current-voltage curve was obtained on the recorder (5 to 10 cycles total).

6. Step 3 was repeated at 80 mV/sec for 2 to 4 min and a current-voltage curve was obtained on the recorder (5 to 10 cycles total). The cycling was stopped when the potential reached 0.4 V (see Figure 5, p. 52).

7. The electrode was left at open-circuit for 10 to 30 sec while the potentiostat was adjusted to the anodization potential for the next experiment.

Steps 1 and 2 had the effect of removing chloride and other gross contaminants from the electrode and the cell. Step 3 was performed to clean the electrode and establish a stable surface as described by Breiter. Step 4 was performed to remove any traces of oxygen film not reduced by cathodic transients to 0.4 V. Step 5 reduced the sweep rate (to meet the requirements of the recorder) to show whether peak stability had been attained and to record the current-voltage curve for the hydrogen adsorption region. Step 6 was performed until the reduction peak height stopped increasing, and a current-voltage curve of the oxygen adsorption and desorption regions was obtained. During the initial evaluation of this pretreatment, current-voltage curves showed the changes described by Breiter (1966). During some of the experiments, small, sharp spikes were observed on the oxygen reduction peaks similar to those described previously by Lingane and Lingane (1963). Changing the sulfuric acid solution and repeating



the pretreatment procedure usually, but not always, eliminated the spikes from the current-voltage curves.

After this study was completed, an additional paper on the subject was published by Biegler (1969) which gave further information concerning the standard pretreatment. Changes in the current-voltage curves during repetitive triangular sweeps were the same as those observed by Breiter (1966). In addition, Biegler showed that the electrode surface could be "roughened" or "smoothed" depending on the type of ac cycling used. Requirements for roughening were an instantaneous reduction step and oxygen coverages in excess of one oxygen atom per surface platinum atom (greater than 1.60 V). It was concluded that triangular sweep cycling did not cause roughening of the electrode surface and that a pretreatment that did not lead to roughening would instead lead to smoothing of the electrode surface. Using the criteria established by Biegler, the electrode standard pretreatment used in the present study would have caused smoothing and a relatively stable surface roughness.

If complete activation is defined as at least 200 cycles between 0.05 and 1.54 V (as in Biegler 1969), an electrode pretreated as described for the present study was not completely activated. Although it was desired to perform the present study with completely activated electrodes, it has not been established that electrode activation is a prerequisite for obtaining valid data of the type involved in this study. Biegler and Woods (1969) determined oxygen coverages using completely activated electrodes. The electrodes were anodized at potentials

between 1.1 and 3.0 V, and the reduction charge was obtained by integrating the current-voltage curves obtained during linear cathodic sweeps. They concluded that their data up to 2.0 V were in good agreement with data obtained by others who did not use pretreatments leading to complete activation.

A basic purpose of the electrode standard pretreatment was to remove all traces of oxygen film formed during previous experiments. A blank correction was obtained by performing the standard pretreatment followed by cathodization for 30 sec at 0.4 V. The electrode was then given the chemical dissolution treatment and the UV spectrum obtained. A shallow absorbance peak was always observed, centered at 262 nm, which was not observed by Peters and Lingane (1962). Also, several investigators have mentioned that some oxygen film is reduced at potentials in the hydrogen adsorption region. It was decided to obtain data to determine if the standard pretreatment left a residual film. The data in Table 2 were obtained on the electrode after it had been standing in deaerated 1 F sulfuric acid for six days to permit any self-discharge mechanisms or diffusion of oxygen from the sublayers to occur. The experiments were performed in the same sequence as they are listed in Table 2. The data in Table 2 should be compared with a typical blank correction of  $A_{230} = 0.020$  and  $A_{262} = 0.030$  with some values up to twice these amounts (see Figure 4). The first value in Table 2 may be due to impurities on the electrode. The next three values indicate that the blank correction might have been lowered by long-term exposure to hot hydrochloric acid and long cathodizations at 0.4 V.

TABLE 2  
 INVESTIGATION OF TRACES OF OXYGEN FILM<sup>a</sup>

Treatment of Electrode <sup>b</sup>	(No Blank Correction)	
	A <sub>230</sub>	A <sub>262</sub>
At open circuit for 30 min in fresh sulfuric acid	0.065	0.046 <sup>c</sup>
10 min at 0.4 V	0.008	0.010
At open circuit for 30 min in fresh sulfuric acid	-0.003	0.002
Cycling 0.4 to 1.4 V for 5 min at 0.4 cps, stopping at 0.4 V	0.026	0.027 <sup>c</sup>
Cycling 0.0 to 0.8 V for 2 min at 0.4 cps, 10 min at 0.4 V, cycling 0.4 to 1.8 V for 5 min at 0.4 cps, stopping at 0.4 V	0.061	0.055 <sup>c</sup>

- a. Platinum electrode, all chemical dissolutions performed in 1 F HCl for one hour at 85-95°.
- b. These experiments were performed in sequence.
- c. These spectra showed a shallow peak centered at 262 nm.

The last two experiments in which the potential was cycled show that small amounts of oxygen may have been left unreduced, but the absorbances observed are about the same amount as the blank correction.

Lauer (1967) proposed a method of obtaining a platinum surface completely free of oxygen film by immersing the electrode in 1 F sulfuric acid at 85° for 5 min. He treated his electrode in the following sequence: (1) reduce the electrode at 0.4 V for an unstated time, (2) oxidize the electrode at 1.45 V for 30 sec at 82°, (3) wait at open circuit for times up to 5 min, and (4) adjust the potentiostat to the potential to which the electrode had drifted and (5) then step the potential to 0.65 V, measuring the cathodic charge for the reduction. No charge was required when the waiting period, step (3), was 5 min. However, the conclusion made is not justified by the experimental data. The anodization was performed at elevated temperature at which the oxygen film may be significantly different from that formed at room temperature. The data in Lauer (1967, Table 3-2) show that when the electrode was cathodized without a waiting period,  $Q_a/Q_c$  was about 4.0 to 4.5 which is a very high value in comparison with ratios between 1.0 to 2.0 obtained by most investigators working at room temperature. If a roughness factor of 1.5 is assumed,  $Q_a = 0.6 \text{ mC/cm}^2$  and  $Q_c = 0.14 \text{ mC/cm}^2$ . The value for  $Q_c$  is much smaller than values observed by other investigators. For comparison, see Gilroy and Conway (1968, Figures 4a and 4b). To evaluate the proposed pretreatment of Lauer, the electrode was given the following treatment: (1) cathodized at 0.4 V for 10 min, (2) anodized at 1.45 V for 30 sec at 25°, (3) placed in 1 F

sulfuric acid at 85° for 5 min, and (4) placed in 1 F hydrochloric acid for one hour. The UV spectrum of the hydrochloric acid was obtained which showed that only 30-40% of the expected oxygen film had been removed by the sulfuric acid step. For this reason, the pretreatment scheme of Lauer (1967) was not used.

As mentioned previously, several investigators have obtained data which they interpreted to show that some oxygen film remains on the electrode after a cathodic treatment. If this were correct, the standard pretreatment chosen for the present study would have been inappropriate. Thus, it seems appropriate to discuss the problem at this time and to list the data obtained to show the adequacy of the standard pretreatment.

Lauer (1967) concluded from his data that Pt(IV) oxide remains unreduced by a cathodic transient, and repetitive ac cycling would cause the residual Pt(IV) to increase to an equilibrium value. As previously shown in Table 2, after cycling between 0.4 and 1.4 V, very little or no platinum was chemically removable. Cycling between 0.4 and 1.8 V gave a small but inconclusive amount of removable platinum. Lauer (1967, p. 57-58) cycled his electrode potential between 0.65 and 1.45 V and observed a decrease in  $Q_a/Q_c$  tending toward unity. To determine if this ac cycling produces a chemically removable oxygen film, as described by Lauer, an experiment was performed during the present study in which the electrode potential was cycled between 0.65 and 1.45 V (stopping at 0.65 V) for 5 min at 0.4 cps (about 120 cycles), and the dissolution procedure was performed. The UV absorption spectrum was

lower than the blank correction. A second experiment was performed during the present study in which the electrode potential was cycled between 0.65 and 1.65 V (stopping at 0.65 V) for 5 min at 0.4 cps (about 120 cycles), and the dissolution procedure again performed. Duplicate results showed that Pt(II) and Pt(IV) had been removed in amounts equivalent to that removed after 30 sec of anodization at 1.65 V. The reason that the oxygen film was not reduced during this cycling was because the oxygen reduction peak had moved to below 0.65 V at this sweep rate and anodization potential. This was confirmed by recording the current-voltage curve.

Feldberg et al. (1963) described a method of forming a "half reduced electrode." An experiment was performed during the present study in which the method of Feldberg was followed, using the prescribed potentiostatic reduction. The chemical dissolution procedure was performed to examine the oxygen film remaining on the "half reduced electrode." The absorbance in the ultraviolet region for the hydrochloric acid was about equal to a blank correction.

It was concluded that the standard pretreatment of our electrodes adequately removes pre-existing oxygen films at least to the extent required by the present study. If the standard pretreatment itself leaves any oxygen film on the electrode surface, the amount must be no more than a few percent of the amount formed during the anodic half-cycles, and the unreduced oxygen film does not build up to detectable amounts. Data obtained to establish the adequacy of the standard pretreatment have been presented in this section of this dissertation

because these data refer specifically to the problem of choosing a pretreatment scheme. Reference will be made to some of these data in a later section of the Discussion because Lauer and Feldberg have proposed that appreciable amounts of oxygen film remain on cathodically reduced electrodes and are the cause of electrode activation.

#### Method of Electrode Area Correction

During the initial stages of this study it became apparent that reproducibility of the data, for Pt(II) and Pt(IV) concentrations, was not as good as desired. In most instances, the reproducibility was  $\pm 10\%$ , but values were obtained that were as low as 60% to as high as 150% of the average values. To reduce any error due to changes in electrode surface area, the pretreatment was altered to include recording the current-voltage curves so that an electrode area correction could be made (see steps 5 and 6 of the standard pretreatment). Previous investigators have measured the "real" area or "roughness" of their electrodes using data obtained from current-voltage curves as described in the review of Gilman (1967, p. 126-136). Although in most cases, the charges passed in the hydrogen adsorption region have been used, there are cases in which use has been made of the charges passed during oxygen film formation or removal.

Biegler (1969) has described a method of determining the roughness factor of a platinum electrode. The charge in the hydrogen adsorption region was measured (by the same procedure mentioned below for  $Q_h$ ) and a charge of  $0.210 \text{ mC/cm}^2$  was defined as being equivalent to one hydrogen per surface platinum atom. Increases in charge above this

value were interpreted as being caused by the "roughness" of the electrode because more platinum atoms were exposed than for a perfectly smooth electrode.

During the present study, the areas under the current-voltage curves were measured with a planimeter, and the corresponding charges were calculated as follows:

1. The hydrogen region charge,  $Q_h$ , was measured between 0.35 V and the start of hydrogen gas evolution at about 0.05 V and "corrected" for double layer charging, etc., by using the current at 0.35 V as the baseline. The current-voltage curve of step 5 of the pretreatment was used (see Figure 1).

2. The anodic oxygen charge,  $Q_a$ , was measured using the anodic current between 0.4 and 1.4 V with zero current as the baseline (see Figures 1 and 5).

3. The cathodic oxygen charge,  $Q_c$ , was measured using the cathodic current between 0.4 and 1.4 V with zero current as the baseline. The current-voltage curve of step 6 of the pretreatment was used to determine  $Q_a$  and  $Q_c$  (see Figures 1 and 5).

In the present study, average values calculated for  $Q_h$ ,  $Q_a$ , and  $Q_c$  were 0.20, 0.58, and 0.51 mC/cm<sup>2</sup>, respectively. For each experimental value of Pt(II) and Pt(IV) concentration, a correction factor was calculated using each of the three measured charges taken during the electrode pretreatment as follows:

$$\frac{Q_{\text{average}}}{Q_{\text{measured}}} = \text{correction factor for electrode area} \quad \text{equation 3}$$



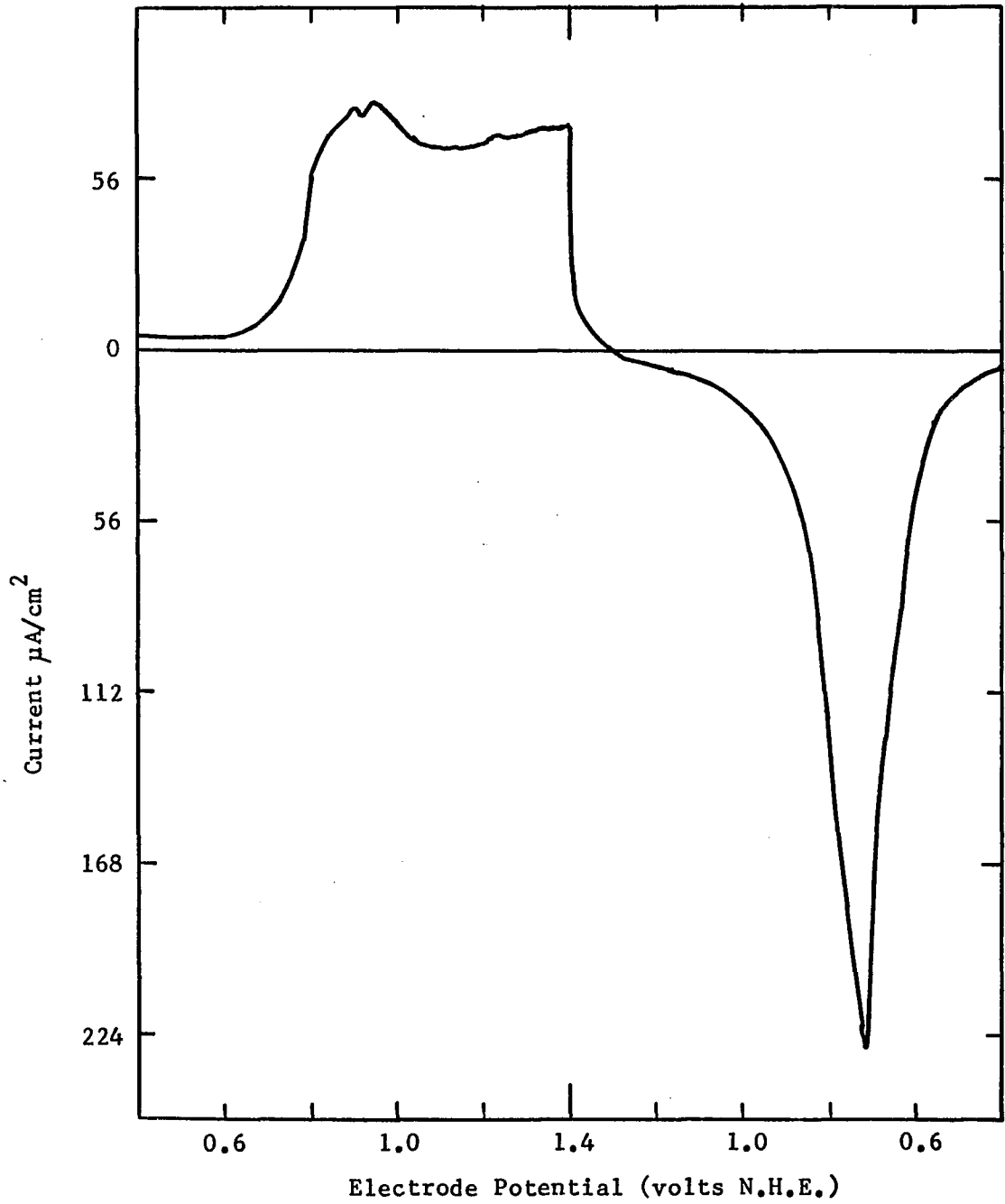


Figure 5. Current-voltage Curve.

(platinum electrode in deaerated 0.5 F sulfuric acid, sweep rate 80 mV/sec)

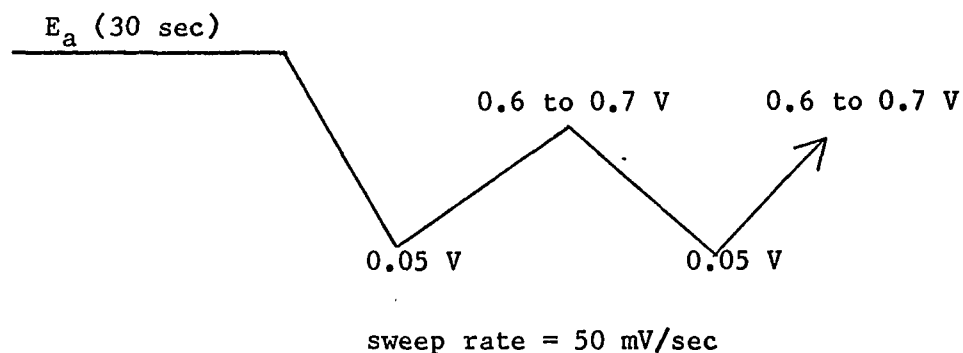
Earlier during the discussion of the pretreatment, it was stated that the charge being passed was probably changing (less than a few percent per cycle) at the time the current-voltage curves were obtained. This, plus the uncertainties in measuring the area of the curves with a planimeter, caused the correction factors to differ from each other by about 10%. The correction factors using the  $Q_a$  values were used because they seemed to correct divergent data more satisfactorily and the use of all three correction factors would have led to three sets of final data not differing essentially from each other. Because the average  $Q_h$  observed in the present study was  $0.20 \text{ mC/cm}^2$ , it is concluded that the roughness factors for the electrode was about unity.

It must be emphasized that this "correction for electrode area" was not entirely justified; i.e., a correction factor was applied to each experimental value based on the charge passed during an anodic transient between 0.4 and 1.4 V which occurred just prior to obtaining the experimental value. It was observed that this charge varied up to  $\pm 20\%$  from the average. There probably is a relationship between the anodic charge passed in a linear sweep to 1.4 V and the amount of oxygen film formed during a 30-sec anodization at the potentials studied. But it is not certain that these two values are directly proportional to each other.

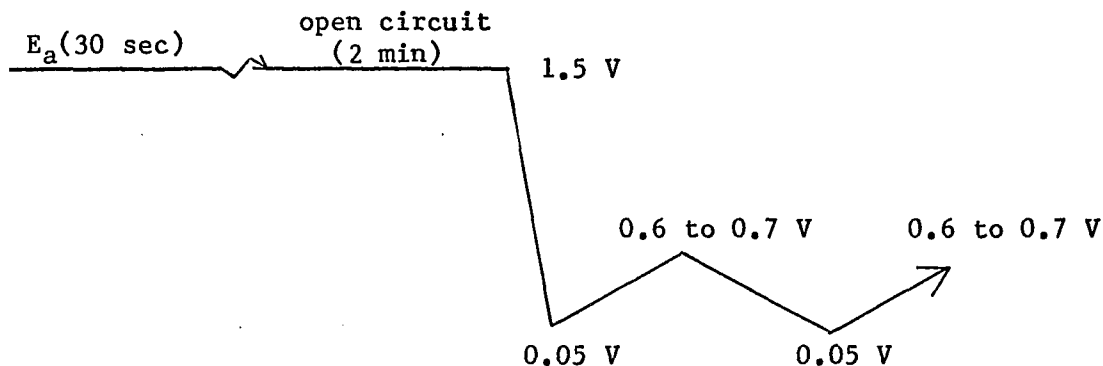
#### Procedure for Determining the Cathodically Reducible Material in the Oxygen Films

The oxygen films were formed by anodizing the platinum electrode for 30 sec at the desired potentials in deaerated 0.5 F sulfuric acid.

Two similar but slightly different procedures for cathodically reducing the oxygen films were used because of the oxygen gas formed at the more anodic potentials. When  $E_a$  was 1.5 V or lower, the electrode was given the standard pretreatment in the electrolysis cell previously described. The electrode was anodized at  $E_a$  for 30 sec, and a linear cathodic sweep at 50 mV/sec was started at  $E_a$ . A current-voltage curve was recorded on the Moseley X-Y recorder. The potential program below was performed.



Because oxygen was evolved at the more anodic potentials, a modified procedure was used when  $E_a$  exceeded 1.5 V. The electrode was pretreated and then anodized for 30 sec in a beaker containing 0.5 F sulfuric acid exposed to the atmosphere. At the end of the anodization the electrode was removed, disconnected from the potentiostat, washed, and inserted in the normal electrolysis cell which had been filled previously with 0.5 F sulfuric acid and deaerated with nitrogen. A rapid flow of nitrogen was maintained until exactly 2 min after step  $E_a$  when the following potential program was performed. The sweep rate was 50 mV/sec.



The modified procedure was required because oxygen was evolved above 1.65 V. When the reduction was attempted in the electrolysis cell after step  $E_a$ , vigorous nitrogen purging for 2 min did not completely remove oxygen from the electrolysis cell. The shape of the cell was not conducive to rapid removal of dissolved gases. A cathodic current between 0.4 and 0.6 V during an anodic transient was considered proof that oxygen had not been removed. The 2-min requirement was used to duplicate the conditions of the chemical dissolution in which the electrode was put into the hydrochloric acid 2 min after the end of the anodization. A second reason for performing the anodization in one solution and the cathodization in another was to avoid any possible complications from electrolysis products other than oxygen. Hydrogen peroxide can be formed from slow spontaneous decomposition of the oxygen film, and ozone can be formed at potentials above 1.55 V (Lauer 1967).

During the cathodic reduction (both modifications of the procedure), the potential was decreased until hydrogen gas evolution had started (at about 0.05 V), and the potential reversed until 0.6 to 0.7 V was attained. During this anodic sweep, the hydrogen adsorbed

during the first cathodic sweep was desorbed. The charge in both of these potential regions was measured with a planimeter, and the two charges always agreed within 10%. The potential was again cycled between 0.6-0.7 V and 0.05 V, and back to 0.6-0.7 V. These second transients were recorded on the same chart paper as the first pair, and only minor differences were observed between the two cycles. Generally, the current during the second cycle was slightly lower (5 to 10%) than during the first cycle.

The purpose of recording these current-voltage curves in the hydrogen adsorption region was to detect any oxygen film that might be reduced in the hydrogen region.

## DATA

### Determination of Pt(II) and Pt(IV) Concentrations by Chemical Dissolu- tion of the Oxygen Film

Oxygen films were formed by anodizing the platinum electrode in deaerated 0.5 F sulfuric acid for 30 sec at potentials between 0.8 and 2.35 V. As stated previously, all potentials are on the standard hydrogen scale and are positive unless otherwise stated. The oxygen films were removed and the concentrations of Pt(II) and Pt(IV) were determined using the procedures described previously.

The individual data obtained for 30 sec of anodization are shown in Table 8 in the Appendix, and the averages of the values obtained at each potential are in Tables 3 and 4 and Figure 6. The data in Table 3 show the steady increase observed in both Pt(II) and Pt(IV) concentrations with limiting values being approached above 2.0 V. The scatter in these data may be partly explained because values were obtained at least every 100 mV over the potential range studied. The increase in the amount of oxygen film caused by increasing the potential by 100 mV is of the same magnitude as the experimental error. At least three determinations were made at each potential to reduce the effect of a single deviant value.

A larger number of values (eight) were obtained at 1.00 V (see Appendix, Table 8) to determine the lowest potential at which oxygen films can be detected by the chemical dissolution technique. At

TABLE 3  
RESULTS OF CHEMICAL DISSOLUTION OF OXYGEN FILMS  
FORMED ON A PLATINUM ELECTRODE<sup>a</sup>

Anodization Potential	C a l c u l a t e d    A v e r a g e s <sup>b</sup>			Total Platinum Concentration
	Pt(II) Conc.	Pt(IV) Conc.	Pt(II)/ Pt(IV)	
Volts (N.H.E.)	F	F		eq/l
1.15	$1.04 \times 10^{-6}$	$3.19 \times 10^{-7}$	3.4	$3.35 \times 10^{-6}$
1.25	$1.70 \times 10^{-6}$	$3.64 \times 10^{-7}$	4.7	$4.86 \times 10^{-6}$
1.35	$2.10 \times 10^{-6}$	$6.47 \times 10^{-7}$	3.4	$6.78 \times 10^{-6}$
1.40	$2.26 \times 10^{-6}$	$7.49 \times 10^{-7}$	3.1	$7.53 \times 10^{-6}$
1.45	$2.43 \times 10^{-6}$	$7.63 \times 10^{-7}$	3.1	$7.91 \times 10^{-6}$
1.55	$2.64 \times 10^{-6}$	$9.40 \times 10^{-7}$	2.8	$9.02 \times 10^{-6}$
1.65	$2.76 \times 10^{-6}$	$7.20 \times 10^{-7}$	3.9	$8.61 \times 10^{-6}$
1.75	$3.05 \times 10^{-6}$	$1.28 \times 10^{-6}$	2.4	$1.12 \times 10^{-5}$
1.85	$3.55 \times 10^{-6}$	$1.25 \times 10^{-6}$	2.9	$1.21 \times 10^{-5}$
1.95	$3.68 \times 10^{-6}$	$1.61 \times 10^{-6}$	2.3	$1.38 \times 10^{-5}$
2.05	$3.80 \times 10^{-6}$	$1.77 \times 10^{-6}$	2.3	$1.47 \times 10^{-5}$
2.15	$4.57 \times 10^{-6}$	$1.78 \times 10^{-6}$	2.6	$1.63 \times 10^{-5}$
2.25	$4.41 \times 10^{-6}$	$1.83 \times 10^{-6}$	2.4	$1.62 \times 10^{-5}$
2.35	$4.66 \times 10^{-6}$	$1.90 \times 10^{-6}$	2.4	$1.69 \times 10^{-5}$

a. Platinum electrodes anodized for 30 sec in 0.5 F sulfuric acid, chemical dissolution in 1 F hydrochloric acid at 85-95° for one hour.

b. See Appendix for individual values.

TABLE 4

COMPARISON BETWEEN METHODS OF REMOVING THE OXYGEN FILM FROM A PLATINUM ELECTRODE

Anodization Potential Volts (N.H.E.)	Column 1 Chemical Data mC/cm <sup>2</sup>	Column 2 Electrochemical Data mC/cm <sup>2</sup>	Reduction Peak Potential Volts (N.H.E.)	Difference Between Column 1 and Column 2 mC/cm <sup>2</sup>
1.00		0.107	0.83	
1.10		0.249	0.84	
1.15	0.226	0.337	0.84	0.111
1.25	0.329	0.408	0.82	0.079
1.35	0.458	0.545	0.77	0.087
1.40	0.509	0.533	0.77	0.024
1.45	0.535	0.623	0.76	0.088
1.50		0.698	0.72	
1.55	0.610	0.704	0.71	0.094
1.65	0.582	0.763	0.69	0.181
1.75	0.758	0.845	0.67	0.087
1.85	0.819	0.959	0.66	0.140
1.95	0.934	1.070	0.64	0.136
2.05	0.995	1.120	0.62	0.125
2.15	1.102	1.270	0.60	0.168
2.25	1.096	1.320	0.60	0.224
2.35	1.143	1.330	0.60	0.187



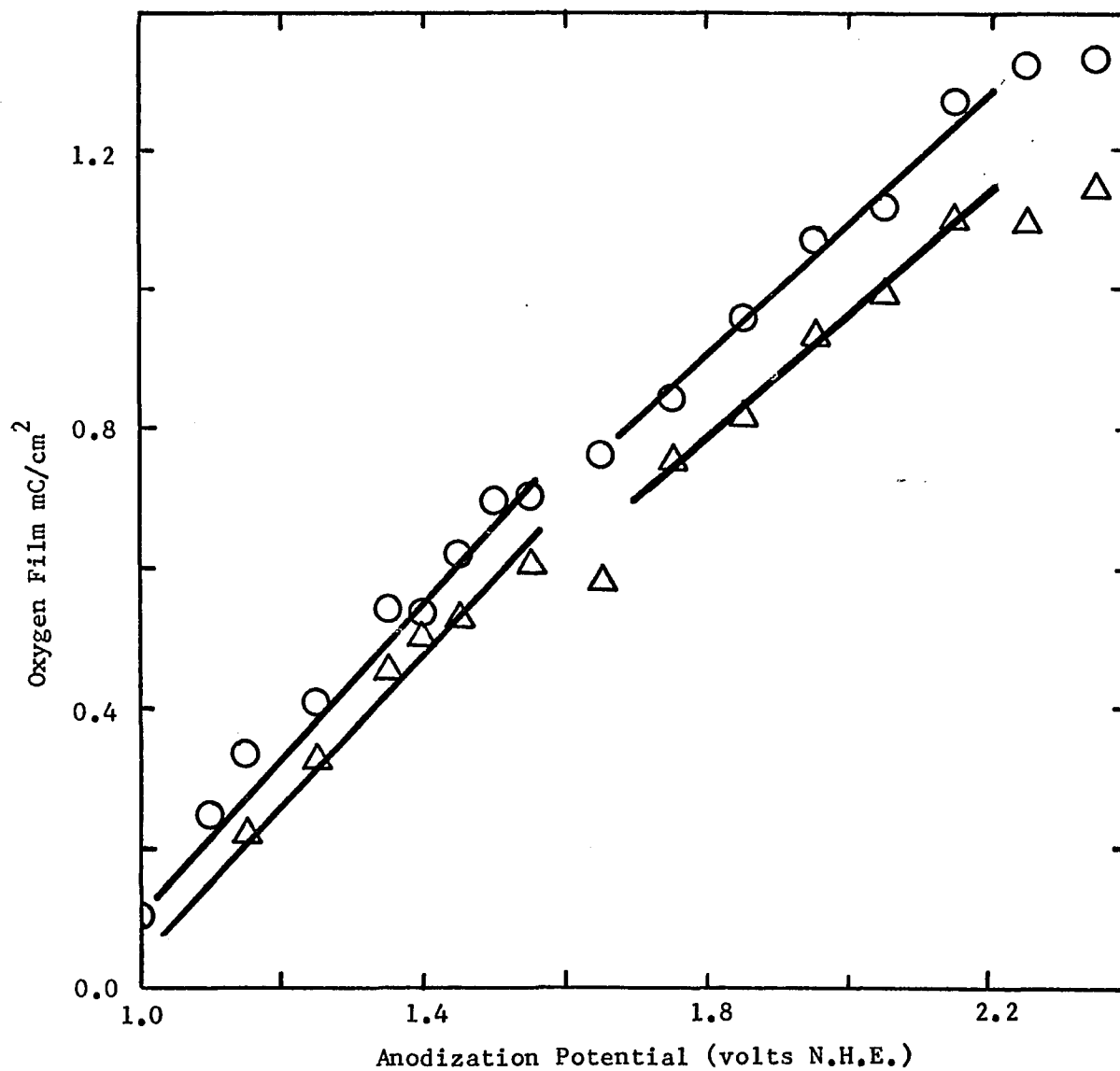


Figure 6. Increase in Amount of Oxygen Film with Anodization Potential.

○ Electrochemical Data  
△ Chemical Dissolution Data

anodization potentials of 1.15 V and higher, the hydrochloric acid solutions always showed measurable concentrations of both platinum ions. However, after anodization at 1.00 V, three of the eight solutions showed measurable concentrations of both platinum ions, three showed no detectable concentrations of either, and the remaining two solutions showed mixed results. If the minimum detectable solution absorbance is defined as 0.030 at both wavelengths, the minimum detectable oxygen film would be  $0.080 \text{ mC/cm}^2$ . The extrapolated chemically removable total platinum at 1.00 V was about  $0.050 \text{ mC/cm}^2$  which is below the minimum detectable amount. For data obtained at 0.95 V, four out of five solutions showed no measurable concentrations of either platinum ion. The data obtained at anodization potentials between 0.80 and 1.00 V are shown in the Appendix, Table 8, and not in Tables 3 and 4, because a calculated average would be of questionable value. The meaning of these results will be discussed later when the existence of a transient platinum-oxygen species is discussed.

The values for the molar ratio of Pt(II)/Pt(IV), listed in Table 3 and shown in Figure 7, show a trend from about 3.5 to 1 at low potentials to 2.5 to 1 at the highest potentials studied. The data are not of sufficient precision to make a clear choice between two conclusions: (a) the molar ratio values decrease linearly over the potential range studied or (b) the molar ratio values decrease to a limiting value of about 2.5 to 1 above 1.6 V. The latter conclusion, not justified by the present data, is suggested by other data discussed in this work which indicate changes in experimental data above 1.6 V.

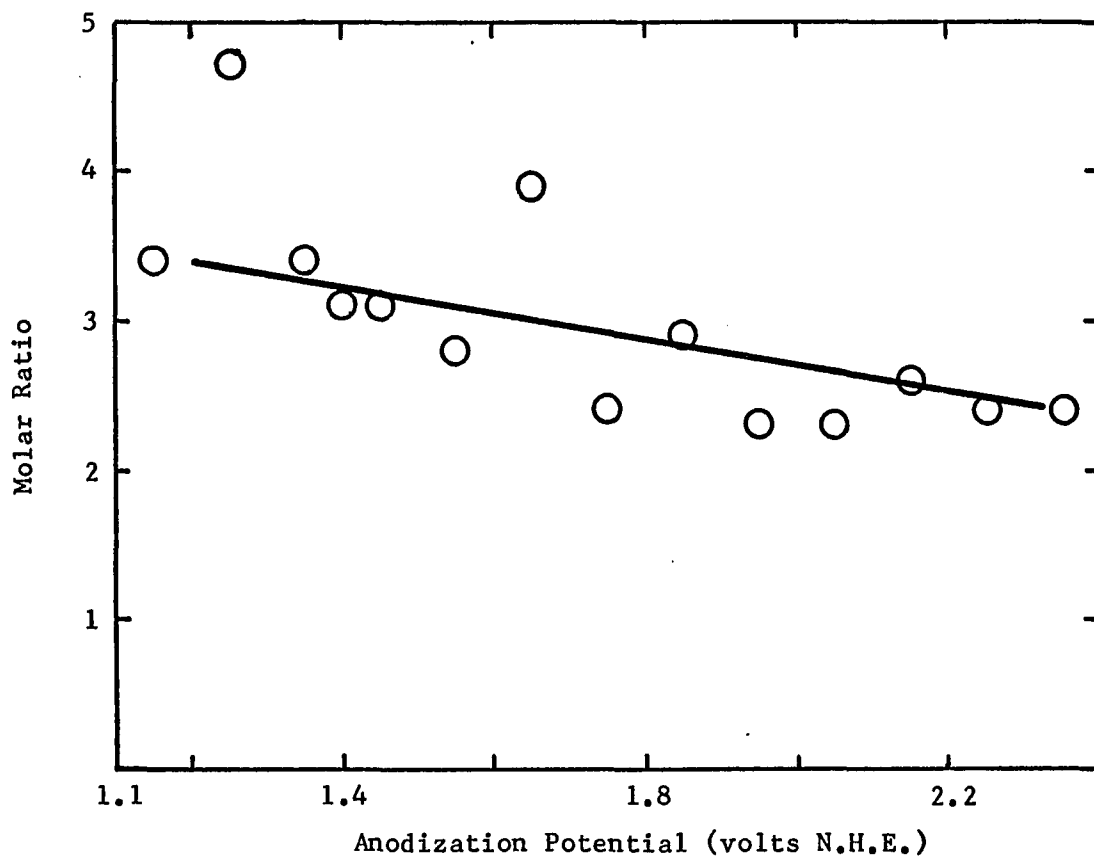


Figure 7. Change in Molar Ratio of Pt(II)/Pt(IV) with Anodization Potential.

The data for the total platinum concentration in eq/l are also shown in Table 3 and Figure 6. They also show an almost linear increase with potential and a limiting value above 2.0 V. A change in the slope for these data is observed at about 1.60 V. The low value for 1.65 V is considered to be due to experimental errors.

Data obtained at 2.50 V have not been included because they were considered invalid. Although the potentiostat was capable of delivering large currents, the electrode used in this study was also large, 14.25 cm<sup>2</sup>. Data at high potentials obtained by other investigators were obtained using small wire electrodes. For example, the electrode used in the present study was over 700 times larger than the electrode used by Biegler and Woods (1969). As a result the current demands placed on the potentiostat may have been excessive at very high potentials. One 30-sec anodization was obtained, but the platinum ion concentrations were about 50% of the amounts usually obtained at 2.35 V. During a 5-min anodization, the current as recorded by the recorder at low sensitivity was observed to vary by as much as a factor of three between the end of the first and the fifth minute. During a 30-sec anodization, the potentiostat fuse failed to carry the current. Another factor to be considered at these high potentials is the effect of the high gas evolution rates upon the potential and current density gradients at the electrode surface. Perhaps one factor causing the oxygen film data to reach limiting values above 2.0 V is an effect of the appreciable gas evolution at these high potentials.

Determination of the Cathodically Reducible Material in the Oxygen Film

The data for the cathodically reducible material were obtained using the method described previously. The data obtained are in Table 4 and Figure 6. The cathodically reducible material (hereafter called "electrochemical data") increases linearly with increased anodization potential up to about 2.0 V. Above this potential the electrochemical data appear to be reaching a limiting value. It should be noted that at an anodization potential of 1.00 V, a readily measured quantity of electrochemically reducible oxygen film was observed. A discontinuity in the data was observed at about 1.6 V as shown in Figure 6. The differences between the chemical and electrochemical data are tabulated in Table 4 and will be discussed in the next section.

The data in Table 4 were obtained by slow reduction, 50 mV/sec, of electrodes anodized for 30 sec. Data were also obtained for longer periods of anodization over the following potential ranges: (a) for 5 min from 1.00 to 2.35 V and (b) for 30 min at 1.95 and 2.15 V. These data were obtained to detect the presence of any oxygen film which was reduced in peaks other than the normal oxygen film reduction peak. In all cases the charge in the hydrogen adsorption and desorption regions were within 10% of each other, and the charge during the second cycle through the hydrogen region was only a little smaller, less than 10%, than that observed during the first cycle. The position and shape of the hydrogen adsorption and desorption peaks were very similar. For the anodization condition of 30 min at 2.15 V, the relative amount of charge passed in the four transients was similar, but during the second

transient through the hydrogen adsorption region, the more anodic hydrogen adsorption peak normally observed was replaced by four smaller peaks. This was the only difference observed in the hydrogen adsorption region. If appreciable amounts of oxygen film were reduced during this potential cycling procedure, differences would have been observed in the current-voltage curves. The small differences observed mean that these abnormal films were not present.

#### Comparison Between the Chemical and Electrochemical Data

Figure 6 and Table 4 show the comparison between the chemical data (from dissolutions of the film) and the electrochemical data (from the cathodic reductions of the film). The data obtained above 1.25 V show that the chemical values are greater than 80% of the electrochemical values.

A calculation of the double layer charging correction, using the data of Laitinen and Enke (1960) showed that this correction was below  $0.030 \text{ mC/cm}^2$  even in the largest cases--the reductions from 1.5 V. Other investigators, such as Gilman (1964), have shown that the values of Laitinen and Enke may be too low, but despite this, the double layer correction is a part but not all of the difference between the chemical and electrochemical data. Because a correction for double layer charging would be small and there is no generally accepted correction, a correction was not made.

The presence of electroactive impurities should have had a greater effect upon the electrochemical data than upon the chemical

data. In both cases, impurities on the electrode surface would have been removed at least partially by the pretreatment. Any remaining impurities probably would not have interfered with the anodization step because oxidizable impurities on the surface should have been quickly removed during the potentiostatic anodization. During the reduction, it is possible that impurities in small amounts could have been reduced without distorting the oxygen reduction peak and thus escaped detection. It is possible, but less likely, that impurities in the hydrochloric acid stripping solution could have reacted with the oxidized platinum atoms of the oxygen film and caused reduction of an oxidized platinum atom to a platinum metal atom or to a complex in solution other than the chloro-complexes.

Data were obtained during the recording of current-voltage curves which may indicate the presence of a transient platinum-oxygen species. As shown previously in Figure 5, the instantaneous current at 1.0 V was 70 to 75  $\mu\text{A}/\text{cm}^2$  during an anodic sweep. This should be compared with typical instantaneous currents at other potentials: (a) between 0.4 and 0.6 V, 4  $\mu\text{A}/\text{cm}^2$ ; (b) at 0.8 V, 30 to 50  $\mu\text{A}/\text{cm}^2$ ; and (c) at 1.4 V, 60 to 70  $\mu\text{A}/\text{cm}^2$ . Secondly, when the instantaneous currents were measured during the 30-sec anodizations at potentials between 0.8 and 1.0 V, the current dropped to less than 3  $\mu\text{A}/\text{cm}^2$  in a few seconds. Although  $Q_a$  was about 10% larger than  $Q_c$ , the amount of charge passed up to 1.00 V was about 25% of  $Q_a$ . It was also observed that the fraction of  $Q_a$  passed before 1.00 V was reached was larger at higher sweep rates. The amount of charge passed before 1.00 V was reached was

about  $0.14 \text{ mC/cm}^2$  which should be compared with the difference between the chemical and electrochemical data. The differences varied from approximately  $0.08 \text{ mC/cm}^2$  at lower potentials to  $0.20 \text{ mC/cm}^2$  at the higher potentials. Clearly, this large amount of charge, which does not lead to a stable oxygen film, is of the same size as the difference between the chemical and electrochemical data.

It is tempting to attribute the difference between  $Q_a$  and  $Q_c$  to the oxidation of impurities to a "condition" in which they are not reduced during the following cathodic transient. It is difficult, however, to explain the large fraction of  $Q_a$  that is passed before 1.0 V is reached. Several investigators have shown that  $Q_c$ , the cathodically reducible material formed below 1.00 V, is very small (see Laitinen and Enke 1960, Morris 1964, and Shibata 1964). It is difficult to attribute all of the above observations to reactions with impurities. The presence of a weakly adsorbed platinum-oxygen species may explain these observations more satisfactorily. A weakly adsorbed oxygen species would be: (a) formed at low potentials without transformation to a more tightly held form and (b) easily removed by self-discharge at potentials below the potential of its formation (this includes open circuit) or by agitation of the solution. Other factors concerning a possible weakly adsorbed platinum-oxygen species will be considered in a later part of the Discussion section of this dissertation.

Another possible explanation of the lower chemical values (compared with the electrochemical data) is the formation of a chemically resistant platinum-oxygen species. Formation might occur at all



potentials and especially at the more anodic potentials. Anson and Lingane (1957) and Breiter and Weininger (1962) observed that 10 to 20% of their oxygen films remained after exposure to their stripping solutions and could be cathodically reduced. In these cases, the oxygen films were formed in sulfuric acid and the dissolution performed in acidic chloride solutions. The amount of undissolved film was determined by cathodic reduction in either sulfuric acid (the former paper) or in the acidic chloride solution (the latter paper). (The reduction of  $\text{PtCl}_6^{-2}$  in acidic chloride solutions could have consumed charge leading to high values for undissolved film.)

These chemically resistant platinum-oxygen species could be just under the metal surface or in a geometric location inaccessible to the chloride ions during the chemical dissolution and yet be readily accessible during electrochemical reduction.

A further possibility is that the chemically resistant species are formed during the dissolution in hydrochloric acid and not during the anodization in sulfuric acid. The formation of mixed oxygen-chlorine films has been described by Peters and Lingane (1962) who observed that films formed in chloride media (pH between 0.1 and 12) were easily and completely removed by heating the filmed electrodes for one hour in 1 F hydrochloric acid. They also observed that the anionic constituents of the film could be easily interchanged. For example, in 1 F hydrochloric acid the film formed,  $\text{PtCl}_2$ , lost all of its chloride by washing the film with water but not with 0.001 F nitric acid. It was concluded that Pt-OH bonds were formed readily from Pt-Cl bonds. The nature of

the films studied by Peters and Lingane (1962) must be considered in any discussion of reactions occurring in hydrochloric acid dissolution procedures.

A final factor to explain the difference between the chemical and electrochemical data, as well as some of the experimental error shown in Appendix Table 8, is the fact that the spectrophotometric determination of the concentrations of the platinum should be less accurate and precise at the lower anodization potentials because the solutions had lower absorbances. For example, the absorbances observed using 10-cm cells were below 0.200 for anodization potentials up to 1.35 V. This analytical method was more effective with the solutions of greater absorbance obtained at the higher anodization potentials which were of more interest during this study (see Figure 4).

#### Miscellaneous Data - Investigation of Hysteresis

The data in the present study were obtained principally by either chemical dissolution or cathodic reduction of oxygen films. After these films were formed, the electrode was at open circuit for 2 min while the electrode was washed and transferred either to the dissolution tube or a second electrolysis cell. Hoare (1965) concluded that  $\text{PtO}_2$  spontaneously decomposed under these conditions. A few experiments were performed during the present study to evaluate this conclusion.

As mentioned earlier, Hoare (1965) obtained some steady-state polarization measurements which were interpreted to mean that  $\text{PtO}_2$  was

formed from Pt-O above 1.8 V. During a cathodic transient the  $\text{PtO}_2$  decomposed to Pt-O and  $\text{O}_2$  before 1.55 V was reached. On further cathodization, no further changes in the oxygen film were said to have occurred because no current flowed until 1.15 V was reached.

During the present study, a pair of experiments were performed in 1 F sulfuric acid (deaerated) in which the electrode was given the following treatment: (1) the standard pretreatment, (2) 10 min at 0.4 V, (3) 30 sec at 2.0 V ( $E_1$ ), and (4) 60 sec at  $E_2$ . During the last step, the potential  $E_2$  was 1.25 V and 1.50 V in the two experiments. In both cases, the current during step  $E_2$  decreased to below  $1 \text{ uA/cm}^2$  within a few seconds. The electrodes were given the dissolution treatment, and the results are shown in Table 5.

The precision of the results is considered fortuitous. These data show that the oxygen film formed at 2.0 V does not decompose to any great extent when the electrode potential is reduced and maintained in the oxygen film formation region. As explained earlier in the Introduction, the hysteresis behavior of oxygen films has not been studied over the entire potential range, and the data in Table 5 are offered to aid others in planning experiments in this area. Actually, these data are compatible with the data of Hoare (1965). His conclusions were based on the concept that Pt-O is formed initially and then, at highly anodic potentials, Pt-O is converted to  $\text{PtO}_2$ . During the reduction transient, no "oxide reduction current" was observed until the potential was reduced below 1.15 V. The conclusion was that any  $\text{PtO}_2$  present must have decomposed. Based on the data presented in the present

TABLE 5  
HYSTERESIS STUDIES

Treatment <sup>a</sup>	Pt(II)	Pt(IV)
	F	F
$E_1 = 2.0 \text{ V}, E_2 = 1.5 \text{ V}$	$4.71 \times 10^{-6}$	$1.62 \times 10^{-6}$
$E_1 = 2.0 \text{ V}, E_2 = 1.25 \text{ V}$	$4.71 \times 10^{-6}$	$1.63 \times 10^{-6}$
$E_1 = 1.95 \text{ V (no step } E_2)^b$	$3.68 \times 10^{-6}$	$1.61 \times 10^{-6}$
$E_1 = 2.05 \text{ V (no step } E_2)^b$	$3.80 \times 10^{-6}$	$1.77 \times 10^{-6}$

a. Platinum electrode in 0.5 F sulfuric acid, chemical dissolution in 1 F hydrochloric acid at 85-95° for one hour.

b. Data from Table 3.

study, these concepts should be modified to feature the concurrent formation of both Pt(II) and Pt(IV) in the oxygen film. Both oxidation states are electrochemically reduced together at low potentials.

Miscellaneous Data -  
Long-Term Anodization

During the present study, experiments were performed to determine whether the molar ratio of Pt(II)/Pt(IV) changed greatly for long anodization times. The platinum electrode was: (1) given the standard pretreatment, (2) anodized at 2.1 V for the desired time, (3) given the dissolution treatment, and (4) finally given a second hour of the dissolution treatment. This last step was performed to determine if all possible dissolution had occurred during the first hour. Data obtained

by others had suggested that "chemically resistant" or "tight oxide" films were formed under highly anodic conditions that might have required extensive exposure to hot hydrochloric acid for their removal. The absorbance values, blank corrected, listed in Table 6 show that the dissolution process was completed during the first hour.

During the present study, experiments were performed to determine the effect of increased anodization time upon the potential of the oxygen film reduction peak. As mentioned earlier, data were obtained between 1.00 and 2.35 V for 5 min of anodization and at 1.95 and 2.15 V for 30 min of anodization. These reduction peak potentials were reproducible to within 10 to 20 mV. The data obtained for anodizations below 1.95 V for 5 min showed that the reduction peak potential was usually less than 20 mV more cathodic than the data obtained after 30 sec of anodization. The data are in Table 7 for anodizations above 1.65 V. These data show a cathodic movement of the reduction peak potential when the anodization potential was above 1.95 V. This effect has not been reported by previous investigators.

TABLE 6  
OXYGEN FILMS FORMED BY LONG-TERM ANODIZATION<sup>a</sup>

Time at 2.10 V min	Pt(II) F	Pt(IV) F	Pt(II)/ Pt(IV)	A b s o r b a n c e			
				First Hour		Second Hour	
				230 nm	262 nm	230 nm	262 nm
0.5	$4.81 \times 10^{-6}$	$1.75 \times 10^{-6}$	2.8	0.439	0.439	0.011	0.006
5	$4.12 \times 10^{-6}$	$2.20 \times 10^{-6}$	1.9	0.401	0.558	0.016	-0.007
20	$6.22 \times 10^{-6}$	$2.16 \times 10^{-6}$	2.9	0.566	0.556	0.007	-0.007

a. Platinum electrode anodized in 0.5 F sulfuric acid, chemical dissolution in 1 F hydrochloric acid at 85-95° for one hour.

TABLE 7  
 VARIATION OF THE POTENTIAL OF THE MAIN OXYGEN FILM  
 REDUCTION PEAK WITH INCREASING ANODIZATION TIME<sup>a</sup>

Anodization Potential (Volts N.H.E.)	Potential of Reduction Peak (Volts N.H.E.)		
	Anodization Time		
	30 sec	5 min	30 min
1.65	0.69	0.67	
1.75	0.67	0.67	
1.85	0.66	0.64	
1.95	0.64	0.62	0.59
2.05	0.62	0.58	
2.15	0.60	0.57	0.54
2.25	0.60	0.55	
2.35	0.60	0.49	
2.50	0.60	-	

a. All anodizations in air-saturated, 0.5 F sulfuric acid and all cathodic reductions performed in deaerated, 0.5 F sulfuric acid at 50 mV/s.

## DISCUSSION

### Validity of Chemical Dissolution Data

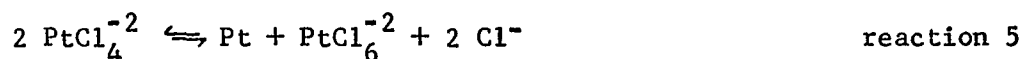
Much of the data in this study were obtained by chemical dissolution of oxygen films. The validity of data obtained by this method is not universally accepted. A thorough discussion of the objections to this method seems appropriate at this point before the discussion of the principal data obtained in the present study.

The chemical dissolution method was first used by Anson and Lingane (1957) and subsequently criticized by Breiter and Weininger (1962). A detailed discussion of these two papers is necessary because numerous reviewers and investigators have used the arguments of Breiter and Weininger to discredit this method and the data obtained using it.

Anson and Lingane (1957) were the first investigators to remove oxygen films from anodized platinum surfaces with hot acidic chloride solutions. They anodized their electrodes using both anodic polarization and chemical oxidizing agents. A stripping solution of 0.2 F HCl and 0.1 F NaCl was used, requiring from 20 to 60 min to remove most of the oxygen film. The longer time was required for electrodes subjected to more severely anodizing conditions. The acidic chloride stripping solutions were analyzed by UV spectrophotometry which showed the characteristic absorption peaks previously established for  $\text{PtCl}_4^{-2}$  and  $\text{PtCl}_6^{-2}$ . They concluded that the presence of these ions and the fact that their molar ratio was 6 to 1 meant that the oxygen film contained



PtO and PtO<sub>2</sub> in a 6 to 1 ratio. They recognized that the presence of both platinum chloro-complexes in the stripping solutions could have been due to a side reaction.

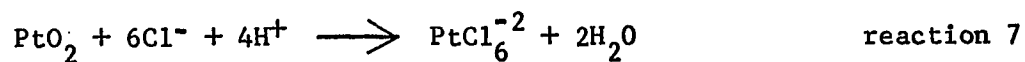
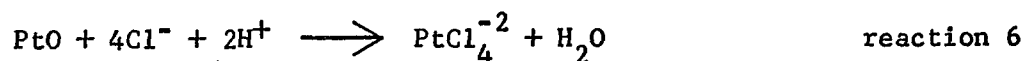


with

$$K = 50 = \frac{(\text{PtCl}_6^{-2}) \cdot (\text{Cl}^-)^2}{(\text{PtCl}_4^{-2})^2} \quad \text{equation 4}$$

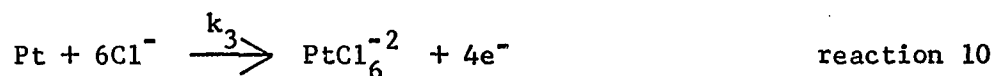
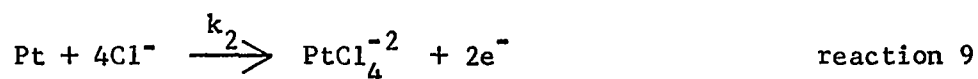
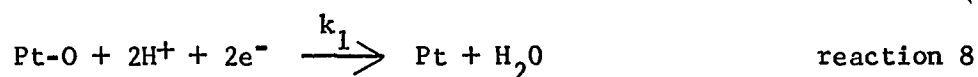
As calculated by Peters and Lingane (1962), in a 1 F hydrochloric acid solution containing  $1 \times 10^{-6}$  F of both  $\text{PtCl}_4^{-2}$  and  $\text{PtCl}_6^{-2}$  initially, at equilibrium the concentrations would be  $3 \times 10^{-6}$  F for  $\text{PtCl}_4^{-2}$  and only  $5 \times 10^{-10}$  F for  $\text{PtCl}_6^{-2}$ . Because of the form of the equilibrium expression and the low concentrations of the two ions initially in the stripping solutions, Pt(IV) should have undergone almost complete reduction by platinum metal to form Pt(II). Because their actual experimental measurements showed that the rate of this reaction is slow, Pt(IV) was observed in solution. Furthermore, the equilibrium expression shows that the Pt(IV) observed in solution could not have come from disproportionation of Pt(II).

The mechanism of Anson and Lingane (1957) for the dissolution reaction was as follows:



The hot acidic chloride solutions removed most but not all of the oxygen film. The residual film was removed by a cathodic reduction. The sum of the charge corresponding to the chemically removed platinum ions plus the residual charge compared favorably with the charge required to cathodically reduce the electrode anodized using an identical procedure.

Breiter and Weininger (1962) disputed the mechanism and conclusions of Anson and Lingane (1957). To support an alternative mechanism, they performed some experiments to show that the dissolution of the oxygen film may explain the presence of the two platinum ions in solution. They described the following mechanism involving a simultaneous cathodic reaction to decompose the oxygen film and two anodic reactions to form the two platinum ions observed in solution,



with the condition that the electrons produced by reactions 9 and 10 are consumed by reaction 8. It should be noted that Pt is a simple, bare platinum atom on the electrode surface in a location different from the sites where reaction 8 is occurring. A careful reading of Breiter and Weininger (1962) reveals that their paper does not mention a Pt\* species as assumed by Lauer (1967), which would be a recently formed bare platinum atom kinetically activated but not thermodynamically different

from any other platinum atom on the surface. It should also be noted that the standard reduction potentials of reactions 9 and 10 are 0.73 and 0.72 V, respectively, at 25°. Because the formation of platinum ions does not occur when a reduced platinum electrode is placed in hot acidic chloride solutions (reactions 9 and 10 are not occurring), platinum ions cannot be formed under these conditions unless a concurrent reduction reaction (reaction 8) is occurring. This mechanism is basically electrochemical involving charge transfer across the electrode-solution interface, while the mechanism of Anson and Lingane is a purely chemical process. However, in any discussion of these proposed mechanisms it must be remembered that the reactions shown are net reactions and that the elementary reactions may be quite different.

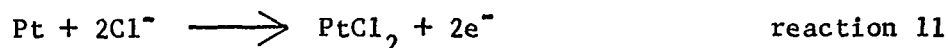
Breiter and Weininger measured the potential of an anodized electrode during the dissolution procedure and also measured the amount of oxygen film remaining on the electrode after exposure to the stripping solution for various times. The rate of dissolution did not have an order of one or higher as expected for a purely chemical process without charge transfer across the electrode-solution interface. The dissolution process did not exhibit a simple reaction order. For example, the dissolution rate was increased threefold when a tenfold more concentrated chloride solution (0.2 F HCl + 2.8 F NaCl) was used. They also measured cathodic charging curves on electrodes with partially removed oxygen films and obtained current-voltage curves during linear potentiostatic sweeps. These data were obtained using electrodes

anodized in sulfuric acid with the measurements being made in acidic chloride solutions.

In summary, the mechanism of Breiter and Weininger describes the dissolution process as a combination of two reactions with the decomposition of the oxygen film, a reduction, obtaining electrons from concurrent oxidation reactions to form the platinum chloro-complexes. The restrictions of this mechanism are very important. Because platinum ions are not formed when reduced platinum metal is placed in hot acidic chloride solutions, the oxidation reactions cannot occur unless the electrons formed can be consumed by a concurrent reduction reaction--the decomposition of the film. This mechanism does not apply if the surface is devoid of bare platinum atoms because the reactions cannot get started until the electrode potential is sufficiently cathodic to permit the reduction to occur. For oxygen films formed at highly anodic conditions where more than a monolayer of film must be present (or each platinum atom is bonded to at least one oxygen atom), it is difficult to describe how the initial bare platinum atoms are formed.

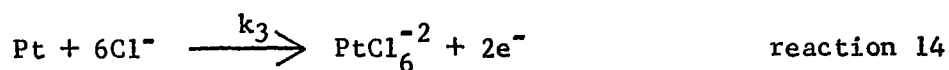
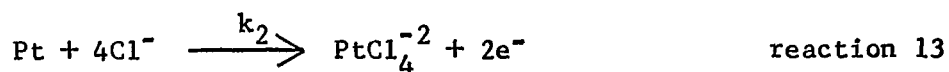
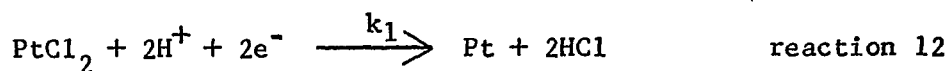
In hot acidic chloride solution, the potential of an anodized electrode quickly decreased to below 1.00 V and, when the dissolution ceased, to 0.75 V. This is the potential range in which the oxygen film is reduced during a cathodic transient. However, the electrode potential must be below about 1.00 V or a platinum-chlorine film would form. Peters and Lingane (1962) formed  $\text{PtCl}_2$  on a platinum surface in 1 F hydrochloric acid ( $30^\circ$ ) between 0.65 and 1.25 V. Although the potential range for this reaction has not been determined at  $85^\circ$ , it is

clear that the electrode potential must be below the potential range of  $\text{PtCl}_2$  formation, or this film would form in preference to platinum ions.



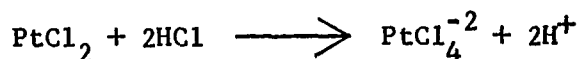
The  $\text{PtCl}_2$  film dissolved completely and quickly in hot acidic chloride solutions, and only  $\text{Pt(II)}$  ions were observed. If the electrode potential were more anodic than required for  $\text{PtCl}_2$  formation, any oxygen film would have been reduced while the oxidation reaction would have been  $\text{PtCl}_2$  formation.

Peters and Lingane did not offer a mechanism for the dissolution of the platinum-chlorine film. A mechanism, similar to the mechanism of Breiter and Weininger, for this process, would require the oxidation of platinum metal to platinum ions to occur at the same potential as the reduction of the platinum-chlorine film when both reactions should be going in the opposite direction. This mechanism would be:



with the third reaction not occurring.

The experimental observations of Peters and Lingane (1962) are more easily explained by:



The data of Breiter and Weininger (1962) showed the electrode potential at the end of the dissolution process to be about 0.75 V. It would be expected that the potential should be in this range for a clean (or nearly clean) platinum electrode in contact with a hot acidic chloride solution containing platinum ions. Either dissolution mechanism (Anson and Lingane or Breiter and Weininger) would give the same result.

The data of Breiter and Weininger (1962, Figures 1, 2, and 5) should be interpreted with caution because the potentials measured or controlled are at 85°. Most data on the reactions that could be occurring are not known at this temperature. The observed data could be affected by platinum-chlorine films which might be present in addition to or instead of platinum-oxygen films.

The weakest point in the mechanism of Breiter and Weininger (1962) is that the rates of reactions 9 and 10 determine the ratio of Pt(II) and Pt(IV) ions found in the stripping solution. The ratio of the two ions was 6 to 1, because the reaction to form  $\text{PtCl}_4^{-2}$  occurred six times faster than the reaction to form  $\text{PtCl}_6^{-2}$ . This feature of the mechanism was undoubtedly prompted by the data of Anson and Lingane (1957) which showed a constant ratio of Pt(II)/Pt(IV) for all oxygen films studied. However, none of the four subsequent investigations using the chemical dissolution method has obtained data in a 6 to 1 molar ratio. These investigations include the present study and three others which will now be discussed.

Every and Grimsley (1965) formed oxygen films in very thick layers (12 to 157 atomic layers) by exposing their platinum electrodes to a very oxidizing medium of fused potassium nitrate at 400° with and without anodization using an external current source. The oxygen films were subsequently dissolved, using the dissolution procedure of Anson and Lingane (1957), and the molar ratio of Pt(II)/Pt(IV) varied between 2.9 and 7.1. When the electrodes were anodized, brown oxygen films were formed faster than when electrolysis was not performed, and the molar ratios were decidedly lower (2.9 to 4.0) for the anodized electrodes.

Lauer (1967) formed oxygen films below 1.65 V in 1 F sulfuric acid, removed them with 0.2 F HCl + 2.8 F NaCl, and used a coulometric procedure to determine the amounts of Pt(II) and Pt(IV) in his stripping solutions. He observed that the sum of the charge equivalent to the stripped platinum ions was equal to the total anodic charge during the anodization. Although some of Lauer's data and conclusions should be confirmed by further work, it is important that he found molar ratios of Pt(II)/Pt(IV) of less than 2 to 1.

A relevant but neglected paper is Peters and Lingane (1962). They formed chlorine and oxygen films in 1.0 F chloride media of varying pH between 0.1 and 12.2. These films were formed by constant current anodization until the electrode potential was about 100 mV below the chlorine or oxygen evolution potential. The electrodes were then analyzed for anionic constituents of the films, and, of interest here, the films were dissolved with 1 F hydrochloric acid. The amounts of

Pt(II) and Pt(IV) ions were determined spectrophotometrically. The film formed in 1 F hydrochloric acid was  $\text{PtCl}_2$  with no evidence for any Pt(IV) ions in the stripping solution. In 1 F sodium chloride solution at pH 7, the molar ratio of Pt(II)/Pt(IV) was 3 to 1. In 5 F sodium chloride at pH 7, the molar ratio increased to 4 to 1. In 1 F sodium chloride at pH 12, the ratio was only 2 to 1. Although these electrodes were anodized in different solutions to different potentials, they were subjected to the same dissolution procedure. In none of these cases was a 6 to 1 molar ratio observed.

The analyses for the anionic constituents of these films showed that films formed in the lower pH solutions contained only chloride and that as the pH was increased the relative amount of oxygen in the film increased. It was concluded by Peters and Lingane that several different chemical bonds were present. The bonds chosen were: Pt - Cl, Pt - OCl, and Pt - OH.

In summary, there is abundant evidence that the molar ratios of Pt(II)/Pt(IV) in these stripping solutions were different for different conditions of film formation. As a result of this fact, the arguments of Breiter and Weininger (1962) are invalid. Further, the slow rate of the interconversion of the two platinum ions after they are in solution show that the varying molar ratios of Pt(II)/Pt(IV) are not the result of reactions occurring after the oxygen film has been dissolved. It is possible that a difference exists in "surface sites" which lead to the two different platinum ions in the solution. It is concluded that the two platinum ions are observed in solution because they are formed in



the chemical dissolution of the film, and the different relative amounts of the two ions are observed because the oxygen films are different. Because two different platinum oxidation states are observed in the stripping solution, it seems reasonable to conclude that different platinum oxidation states are present in the oxygen films. Because the ratios of Pt(II)/Pt(IV) vary over a wide range, it seems highly unlikely that they formed from the same platinum species in the film.

#### Molar Ratio of Pt(II) to Pt(IV) in the Oxygen Film

The data obtained in the present study show that the molar ratio of Pt(II)/Pt(IV) in the oxygen film varied from about 3 or 4 to 1 at potentials up to about 1.4 V to about 2 or 3 to 1 at the highest potential studied, 2.35 V. The increase in the relative amount of Pt(IV) is gradual with increased anodization potential. The fact that Pt(IV) is present even in oxygen films formed at the lowest potentials (at which an oxygen film is formed), and the molar ratio of Pt(II)/Pt(IV) decreases only gradually with increased anodization potential, is an indication that the energy and kinetic requirements to form the two platinum oxidation states are very similar in sulfuric acid solutions.

These conclusions contradict the conclusions of other investigators who have proposed a sequential scheme for formation of the various "platinum oxides." For example, Mayell and Langer (1964, p. 440) concluded: "It appears then that the platinum surface is altered in steps and that each stage begins, approximately, after the preceding state is terminated." They plotted the cathodically reducible material

vs. the potential to which the electrode was oxidized (for both constant current and constant potential operations) and noted that the plot was linear over certain discrete potential ranges. At the end of each discrete range, the charge required to reduce the electrode was compared with the calculated charge for each electron in a reaction to cover a monolayer of smooth platinum (from the number of platinum atoms on the surface). The number of electrons involved per platinum atom was calculated. For example, the charge required to reduce the electrode when anodized (constant current) to 1.24 V was two electrons per surface platinum atom or to a  $\text{Pt}(\text{OH})_2$  monolayer. At 1.54 V, the charge corresponded to four electrons per platinum atom which was interpreted as being conversion of the  $\text{Pt}(\text{OH})_2$  monolayer to a  $\text{Pt}(\text{O})_2$  monolayer. Similar comparisons were made at higher potentials and for data obtained following constant potential anodization. The rest potential of the electrode was determined after each anodization, and this rest potential was assigned to the surface oxidation state.

The concept of monolayer formation is not generally contested, but rather the nature of the monolayer itself. The concept of a layer of Pt(II) bonded to an average of one oxygen species being converted to a layer of Pt(IV) bonded to an average of two oxygen species is not supported by the data of the present study or other recent work. Finally, the measurement of the rest potentials after anodization and the comparison of these values with those which have been assigned to various platinum oxides lead to conclusions of marginal value. A particular rest potential can be explained by several equally satisfactory

reactions and/or surface compounds. The reverse process of determining the reactions and/or surface compounds to explain the rest potential is good confirmatory evidence that correct decisions have been made.

The data of Mayell and Langer (1964) are not particularly useful because the anodization conditions were improperly chosen. Their basic conclusion, which is also held by other investigators, that a monolayer of  $\text{Pt}(\text{OH})_2$ , which was formed upon anodization to 1.24 V, is converted to a monolayer of  $\text{PtO}_2$  upon anodization to 1.54 V should be discarded. A new concept is required involving concurrent oxidation of the platinum atoms on or just under the surface to both Pt(II) and Pt(IV) with the oxygen layer consisting of the corresponding number of oxygen atoms.

The data of the present study and of Biegler and Woods (1969) show that the cathodically reducible material increases linearly with potential (for constant potential anodization) and corresponds to several electrons per surface platinum atom. Biegler and Woods interpreted their data to describe an oxygen film consisting of up to 2.66 oxygen atoms per surface platinum atom chemisorbed on the surface when a "complete monolayer" is formed above 2.0 V. This value of 2.66 oxygen atoms per surface platinum atom should be compared with the data in Table 4. If the roughness factor of our electrode is assumed to be unity, the charge corresponding to one oxygen atom per surface platinum atom would be  $0.42 \text{ mC/cm}^2$ . The limiting values being approached by the data in Table 4 would correspond to about 3.2 oxygen atoms per platinum atom for the electrochemical data and 2.8 for the chemical data.

The data obtained by chemical dissolution (Table 4) show that the total amount of removed platinum atoms agrees, within experimental limitations, with the charge required to reduce the oxygen film. These data also show that more than a monolayer of platinum is removed from the surface during chemical dissolution when the oxygen film consists of more than one oxygen atom per surface platinum atom. Biegler and Woods (1969) presented good arguments supporting the concept of a chemisorbed oxygen layer above the platinum surface with little or no dermasorption when their "complete monolayer" was formed. But when a film of this description is removed by chemical dissolution, some of the removed platinum atoms must have come from below the surface, i.e., from platinum layers which were not involved in the bonding to oxygen. Thus, the platinum atoms which enter solution must come from two sources: (a) those involved in the chemical bonding on the surface and (b) those in the first few sublayers. This chemical dissolution could form varying ratios of the two platinum ions in solution if the reactions to form the two platinum ions have different rates when the substrate is a surface platinum atom bonded to oxygen or a sublayer platinum atom.

The concept of a "complete monolayer" of 2.66 oxygen atoms loosely bonded to each surface platinum atom (on the average) would require the transfer of an average of 5.33 electrons per surface platinum atom in highly distorted orbitals. If sublayer platinum atoms are not involved in electron donation, the average positive oxidation state of the surface platinum atoms must be quite high. Pt(VI) in  $\text{PtO}_3$  has been reported to spontaneously decompose in water. It is difficult to reconcile an unstable oxygen film formed with platinum atoms in high formal

oxidation states, with experimental observations showing the enhanced stability of oxygen films formed at high potentials relative to those formed at low potentials. As discussed earlier, hysteresis studies have given information describing film stability. Oxygen films formed at 1.5 V are partially decomposed if the potential is decreased to 1.2 V, but oxygen films formed above 1.7 V retain their cathodically reducible material when the potential is reduced to 1.5 V. Although additional hysteresis studies should be performed before a conclusion is made, the available data do not lead to the conclusion that oxygen films formed at high potentials are less stable than those formed at low potentials. With regard to oxygen film stability in hot acidic chloride solutions, Anson and Lingane (1957), Breiter and Weininger (1962), and Every and Grimsley (1965) agree that film stability increases with increased severity of anodization. Finally, the electrochemical data in the present study (and elsewhere) show that the oxygen film reduction peak moves cathodically for increasing anodization potentials and for increasing length of anodization.

The concept of a "complete monolayer" of chemisorbed oxygen species above the platinum surface is difficult to reconcile with experimental data showing disruption of the platinum surface by ac cycling. The data of Anson and King (1962) and Hoare (1964) are examples of visible effects caused by repeated ac cycling. In addition, the data of Kozawa (1964) and Every and Grimsley (1965) show the formation of thick oxygen films (more than ten oxygen atoms per surface platinum atom) under extreme conditions of anodization. These two types of data,

the disruption of the surface by ac cycling and the formation of thick oxygen films under extreme conditions, are more easily explained if at least some oxygen is present below the surface platinum atoms in all oxygen films--even those formed below 1.6 V.

The data which prompted this study, obtained by Ramaley and Laitinen (1966), showed reduction peak separation during rapid cathodic reduction of oxygen films formed above 1.6 V. These data, supported by the data of Gilroy and Conway (1968) and Will and Knorr (1960), showed that the oxygen films formed above 1.6 V were different than those films formed below 1.6 V in the manner of their electrochemical reduction.

In the present study, the total amount of oxygen film (obtained by both electrochemical reduction and by chemical dissolution) and the molar ratio of Pt(II)/Pt(IV) show that the two types of film do not differ greatly in the oxidation state of platinum in the platinum-oxygen bonding. The concept of a chemisorbed oxygen layer above the platinum surface does not lead to a satisfactory explanation of the reduction peak separation. The observed reduction peak separation does lead to the conclusion that there are two different types of platinum-oxygen bonding present with the more easily reducible (first type) formed at all potentials and the less easily reducible (second type) formed above 1.6 V. These two types correspond to the two reduction peaks formed during fast reduction. During slow reductions, the second type is converted into the first type, and they are reduced together in a single peak.

The existence of an interconversion process is postulated because it is the simplest but not necessarily the only explanation of the observed behavior. Only a few facts concerning this process are available. First, the time required for the process is in the range below 100 msec. If sufficient time is available during a cathodic transient, the second type of oxygen film is converted into the first type, and only one reduction peak is observed. When sufficient time is not available, the interconversion process is only partially completed during the first reduction peak, and two reduction peaks are observed. Secondly, the interconversion process is not a Pt(IV) to Pt(II) reduction. The data showing very similar ratios of both platinum species in the oxygen films formed at all potentials rules out this explanation. Thirdly, the interconversion process causes or is accompanied by a smoothing of the electrode surface. The data of Gilman (1965) and Biegler (1969) showed that very rapid reductions caused surface roughening while slower reductions caused surface smoothing. Biegler (1969) also observed an increase in roughening rate when the time and potential of anodization were increased.

These facts lead to the conclusion that conversion of the second type to the first type of oxygen film is probably not occurring in an oxygen film above the platinum surface but rather in the first few layers below the surface. During slow reductions, the platinum-oxygen bonds above the surface are reduced first, and the sublayer oxygen species have sufficient time to move to the surface for reduction. During rapid reductions, the movement of sublayer oxygen species to the surface

is too slow, and they are reduced below the surface or brought to the surface and reduced in the second of the two reduction peaks. In the slow reductions, the surface is less disturbed by this movement of oxygen species than it is during the rapid reductions.

The molar ratios of Pt(II)/Pt(IV) obtained in the present study are significantly lower than those obtained by Anson and Lingane (1957). This earlier paper omitted information concerning several important experimental factors. Although the extent of conversion of  $\text{PtCl}_6^{-2}$  into  $\text{PtCl}_4^{-2}$  was mentioned, it is not certain whether a correction was applied. In the acidic chloride stripping solutions, the low absorbance values at 262 nm [where Pt(IV) absorbs] observed by Anson and Lingane did not require a correction for the absorbance of Pt(IV) at 230 nm where Pt(II) absorbs. Failure to make this correction would yield high values for Pt(II) and for the Pt(II)/Pt(IV) molar ratios. Another experimental difference was in the method of electrode pretreatment as discussed earlier.

The principal difference was in the method of anodization. Anson and Lingane performed the following anodizations: (a) a constant current sweep until 1.48 V was reached, (b) a constant current of 0.033 mA/cm<sup>2</sup> for 5 min (the potential was undoubtedly in the oxygen evolution region), and (c) standing the electrode in solutions of several oxidizing agents for 5 min. In addition, the constant current anodizations were performed with the indicator electrode (60 cm<sup>2</sup> both sides) and a single counter electrode facing each other in a cell. The current



density and potential gradients across the front and back sides of the electrode would have been different and unknown.

These experimental factors in the work performed by Anson and Lingane (1957) differed from the ones used in the present study. The effects of these factors and others have not been determined on either the amount of oxygen film formed or on the molar ratio of Pt(II)/Pt(IV).

In summary, the data in the present study for the molar ratio of Pt(II)/Pt(IV) show that a mixture of both platinum oxidation states are formed, over the potential range at which oxygen films are formed, with slightly lower ratios [relatively more Pt(IV)] at higher anodization potentials. The data for total amount of oxygen film show a linear increase up to about 2.0 V and a limiting value above this potential. These two facts, the molar ratio and amount of film, do not explain the differences in data obtained for formation kinetics, reduction kinetics, film stability, etc. for oxygen films formed above and below 1.6 V. It is concluded that the explanation of these phenomenon (formation kinetics, reduction kinetics, film stability, hysteresis behavior, mechanism of the activation process, etc.) does not involve attributing the differences observed to either Pt(II) or Pt(IV) exclusively. The observed behavior of the oxygen films formed under different conditions should be explained, using models involving factors other than the platinum oxidation state. For example, the mechanism of electrode surface activation should not involve only Pt(IV)-oxygen bonds or a surface after their reduction. The activation mechanism should describe the surface after the reduction of both

Pt(II) and Pt(IV) in the oxygen film. Similarly, the kinetic explanation of oxygen film growth and removal should not involve only differences in the rates of reactions of the two oxidation states, but rather the explanation should involve perhaps two similar films (from the platinum oxidation state standpoint) located above and below the surface or in some unusual structure above the surface.

#### Existence of a Weakly Adsorbed Platinum-Oxygen Species

As mentioned earlier in the Introduction section of this dissertation, the work of Shibata (1964) and some data of the present study point to the existence of a weakly adsorbed platinum-oxygen species which becomes loosely attached to the electrode surface. The existence of a weakly adsorbed platinum-oxygen species is not generally accepted, and only a few investigators have devised experiments to obtain information to clarify this subject. While a concerted effort to detect or to describe this weakly adsorbed species was not a goal of the present study, some information was obtained and is included in this dissertation for the purpose of re-opening interest in this subject and aiding other investigators in devising and planning future experiments.

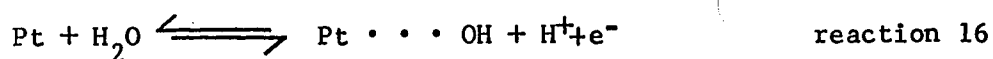
The existence of a weakly adsorbed platinum-oxygen species is most easily detected at low potentials below the potential at which a stable oxygen film is formed. This weakly adsorbed species may be formed at all anodization potentials and may act as a precursor to a more stable platinum-oxygen bond. During the present study, a series of slow triangular potential sweep experiments were performed in which

the most anodic potential,  $E_a$ , was slowly increased in the range between 0.90 and 1.05 V. Just before potential reversal, the anodic current was observed to increase without an appreciable increase in current between 0.80 and 0.85 V during the cathodic cycle. (Table 4 shows that the oxygen film formed during potentiostatic anodization between 1.00 and 1.25 V is reduced in a broad peak centered between 0.80 and 0.85 V.)

As shown in Figure 5, during a linear anodic transient the instantaneous current is appreciable at potentials as low as 0.80 V, and the current is higher at 1.00 V than at potentials up to 1.50 V. Also during transients between 0.40 and 1.40 V, the difference between  $Q_a$  and  $Q_c$  is only 10% while the fraction of  $Q_a$  passed before 1.00 V is 25% of the total, or about  $0.140 \text{ mC/cm}^2$ .

The data of the present study (Table 4) show that the differences between the chemical and electrochemical data were fairly constant in the low potential region below 1.5 V. Two factors already considered as causes of this difference, double layer charging and formation of chemically resistant oxygen film, should have decreased in magnitude for the lower potential anodizations. Yet, the difference does not decrease. A possible factor is the existence of a weakly adsorbed platinum-oxygen species. As stated earlier, the difference between  $Q_a$  and  $Q_c$  in this study was about  $0.070 \text{ mC/cm}^2$ , of which a portion could be attributed to a transient species which leaves the electrode surface between cycles without being reduced. This species could have been removed by the extensive washing of the electrode

between the electrolysis step and the chemical dissolution step. The electrochemical data obtained below 1.50 V were obtained without washing the electrode. For the higher potential anodizations above 1.50 V the effect of the transient species may be too small to be observed. During ac cycling the amount of this weakly adsorbed species, which leaves before the potential is sufficiently cathodic to permit its electrochemical reduction, would be a fraction of the total amount formed depending upon pH, temperature, sweep rate, agitation, etc. During the first stage of multiple ac cycling, the other factors affecting  $Q_a$  and  $Q_c$  (such as impurity desorption from the surface, reactions with solution impurities, and possibly others) are also proceeding and reaching a steady state. During an anodic transient, the potential of the initial current passage moved cathodically about 60 mV for each tenfold decrease in acidity. The reaction occurring (possibly the formation of this weakly adsorbed species) should release one mole of hydrogen ion per faraday. Finally, the current-voltage curves in 0.5 to 1.0 F sulfuric acid show a large current increase at about 0.95 V during the first few dozen cycles of multiple ac cycling (see Breiter 1966 and Biegler 1969). Because stable oxygen films (capable of being dissolved in hot acidic chloride solution) are not formed at this potential, this current increase could be caused by formation of the weakly adsorbed species. The reaction could be:



with the dotted bond indicating a very weak interaction easily broken merely by solution stirring. There are many oxidative decomposition products of water that could be formed, but it is difficult to devise an experiment to determine the nature of these species. The formation of stronger bonds could require a slightly more anodic potential [such as the current increase at 1.07 V observed by Biegler (1969)] with the onset of forming an appreciable number of more stable bonds at about 1.00 V. The data of the present study suggest this. The ellipsometric data of Reddy, Genshaw, and Bockris (1964) show the formation of a new phase on the platinum surface at 0.98 V in 0.5 F sulfuric acid.

Although more experimental work should be done to prove the existence of this weakly adsorbed species, the data obtained in the present study and in the papers referenced in this section are more easily explained if a weakly adsorbed species is used.

#### Activation of Platinum Electrode Surfaces

Although the investigation of the process of electrode activation was not a major goal of the present study, some information was obtained concerning the various theories extant explaining this process.

Feldberg et al. (1963) proposed a "half-reduced oxide layer" which possessed enhanced activity toward oxygen gas in acid solution according to their data. During the present study an attempt to form the "half-reduced oxide layer" according to their directions was unsuccessful (no chemically removable platinum ions were observed). Taking into consideration the criticisms of this proposed activation procedure by James (1967), it is concluded that the half-reduced oxygen

film does not exist, and that the experimental data in Feldberg et al. (1963) are better explained in other ways.

Mayelland Langer (1964) concluded that a "tight oxide" formed on smooth platinum at highly anodic potentials above 1.70 V because they observed a decrease in the cathodically reducible material above this potential. They postulated that oxygen bridges were formed which linked every surface platinum atom and sealed off the electrode surface. This protective film made the electrode surface more stable and relatively inert. The chemical and electrochemical data of Table 4 did not show the formation of the "tight oxide." The chemical dissolution data for total platinum in the oxygen film showed that oxygen films formed up to 2.35 V are not chemically inert to hot acidic chloride solutions. The amount of oxygen film increased linearly with potential up to about 2.0 V.

Lauer (1967) proposed that electrode activation was the result of oxide, specifically the Pt(IV) oxide, remaining on the electrode surface after an ac treatment. Attempts made during the present study to prepare surfaces activated according to this theory showed very little or no chemically removable platinum on electrodes given an ac treatment. If the Pt(IV) oxide were nonelectroactive, it should have remained on the electrode surface after extensive cycling between 0.40 and 1.40 V. This was not observed. Cycling between 0.65 and 1.65 V did result in residual oxygen film [of the same Pt(II)/Pt(IV) molar ratio as observed for anodizations up to 1.65 V], but this was due to movement of the reduction peak to below 0.65 V at the sweep rates

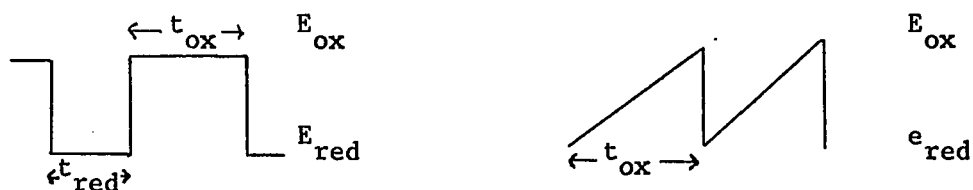
employed. It is concluded that if Pt(IV) remained on the electrode after a proper ac treatment, the amount was below the minimum detectable amount for the chemical dissolution procedure.

James (1967) has concluded that the chief benefit of brief anodizations or ac treatments is the removal of impurities from the electrode surface and that more lengthy and severe anodizations will produce a more permanent electrode activation. These latter activation procedures were not investigated in the present study because (a) Hoare (1965) has described the excellent stability of his Pt-O alloy electrodes toward long-term cathodization, and the oxygen film formed above the alloy surface is probably very similar to that formed on a bare platinum surface and (b) the thick oxygen films (with the unusual oxygen film reduced at 0.20V during slow cathodization) of Shibata (1963) and Kozawa (1964) required constant current equipment for their proper formation. The only pertinent information obtained was that the presence of the 0.20 V reduction peak was not detected in the films formed in the present study.

The view that brief anodizations or ac treatments serve primarily to remove surface impurities was considered in choosing the method of electrode pretreatment and in preparing the sulfuric acid electrolyte.

Biegler (1969) has recognized that contaminant adsorption is an important factor in electrode deactivation, but he has interpreted his data to strengthen the view that structural changes are also important. Stated briefly, his mechanism of electrode activation is the

formation of a stable surface of low index crystal faces during ac cycling. The activity of this surface is long-lived unless contaminant adsorption occurs, and the original activity is readily restored by contaminant removal. An important feature is the suggestion that electrode activation and surface roughening occur by the same mechanism with roughening occurring when the conditions for activation are extended. The requirements for roughening were (a) an oxygen/platinum ratio exceeding one (the Pt-Pt bonds are weakened if the surface platinum atoms are bonded to more than one oxygen atom), and (b) the reduction is fast. The ac treatments found to cause roughening were as follows:



When the second treatment was used roughening was not observed when  $E_{ox}$  was 1.54 V but was observed when  $E_{ox}$  was 1.67 V. The roughening rate increased when  $E_{ox}$  was increased above 1.67 V. It is clear that the conditions required for roughening are similar to those employed by Ramaley and Laitinen (1966) when they observed the reduction peak separation. If the interpretation of the two reduction peaks observed by Ramaley and Laitinen is correct that two different types of oxygen film are present (perhaps one above and one just below the surface platinum atoms), then roughening occurs only when the second more cathodic reduction process occurs. If this process is the reduction of



oxygen species below the platinum surface atoms, the residual platinum surface should be in a state of disarray. If the next anodic transient occurs before the surface rearranges, the repetition of this process (deposition of some of the oxygen species below the surface followed by their reduction below but not above the surface) would lead to surface roughening.

### Conclusions

In the Introduction section of this dissertation, several research goals were established. The molar ratio of Pt(II)/Pt(IV) in the oxygen film varied from 3 or 4 to 1 at anodization potentials up to about 1.40 V to about 2 or 3 to 1 at the highest potential studied, 2.35 V. Data were obtained for anodization potentials between 1.15 and 2.35 V.

The additional goals which were established will now be discussed, using the same numbering system as appeared previously for clarity.

1. The amount of oxygen film formed by anodizing the platinum electrode for 30 sec was determined by cathodically reducing these films. The amount of film increased linearly with increased anodization potential up to about 2.00 V. Above this potential, a limiting value of about  $1.33 \text{ mC/cm}^2$  was being approached.

2. The amount of oxygen film removed by chemical dissolution was determined by calculating the charge equivalent to the amount of platinum ions in the stripping solutions. These data showed a linear increase with increased anodization potential up to about 2.00 V.

Above this potential, a limiting value of about  $1.15 \text{ mC/cm}^2$  was being approached. For anodization potentials above 1.25 V, the chemical data were in good agreement with the electrochemical data. This supports the conclusion, but does not absolutely prove, that chemical dissolution is a valid method of obtaining information concerning the oxygen films on platinum electrodes.

3. The lowest anodization potential at which oxygen films are formed in 0.5 F sulfuric acid was different for the two methods of removing the film. For the electrochemical method,  $0.107 \text{ mC/cm}^2$  of oxygen film was observed for anodization at 1.00 V. For this potential, the chemical data showed about  $0.050 \text{ mC/cm}^2$  of film (by extrapolation) which was below the minimum detection limit ( $0.080 \text{ mC/cm}^2$ ) for this method. At an anodization potential of 1.15 V, the chemical data showed  $0.226 \text{ mC/cm}^2$  of oxygen film. Additional data were obtained and arguments presented to show that these data showed the possible presence of a weakly adsorbed platinum-oxygen species.

4. Exposure of anodized electrodes to hot 1 F hydrochloric acid for one hour was sufficient to remove all of the film removable by this technique. After anodizations above 1.25 V, the amount of film removed was between 80 and 95% of the amount of film reducible by a cathodic transient. Exposure of the anodized electrodes for a second hour did not remove appreciable amounts of oxygen film.

5. It was shown that cathodic reduction transients can leave oxygen film on anodized electrodes if the sweep rate is too fast or the most cathodic potential is not low enough. If experimental conditions

result in the movement of the oxygen film reduction peak to potentials more cathodic than the cathodic reduction transient, some of the film will not be reduced. Two previously known experimental conditions causing movement of the reduction were sweep rate and the formation potential of the film. In addition, it was established that length of anodization at potentials above 1.95 V also caused movement of the reduction peak.

It was concluded that chemical dissolution of oxygen films was a valid method of obtaining information concerning these films. The data obtained by this method compared reasonably well with data obtained by electrochemical reduction of oxygen films. In addition, information previously published by other investigators was evaluated to lend support to this conclusion.

APPENDIX

STATISTICAL DATA

TABLE 8

INDIVIDUAL VALUES OF RESULTS OF CHEMICAL DISSOLUTION  
OF OXYGEN FILMS FORMED ON A PLATINUM ELECTRODE<sup>a</sup>

Anodization Potential Volts (N.H.E.)	Pt(II) Conc. F	Pt(IV) Conc. F	Molar Ratio Pt(II)/ Pt(IV)	Pt <sub>total</sub> eq/l
0.80	$< 3.5 \times 10^{-7b}$	$< 1.2 \times 10^{-7b}$		
	$< 3.5 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		
0.90	$< 3.5 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		
	$< 3.5 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		
0.95	$< 3.5 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		
	$4.41 \times 10^{-7}$	$1.6 \times 10^{-7}$	2.8	$1.52 \times 10^{-6}$
	$< 3.5 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		
	$< 3.5 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		
	$< 3.5 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		
1.00	$1.34 \times 10^{-6}$	$1.7 \times 10^{-7}$	7.9	$3.04 \times 10^{-6}$
	$< 3.5 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		
	$6.2 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		
	$3.93 \times 10^{-7}$	$< 1.2 \times 10^{-7}$		

TABLE 8.--Continued

	$1.36 \times 10^{-6}$	$3.12 \times 10^{-7}$	4.4	$3.96 \times 10^{-6}$
	$1.05 \times 10^{-6}$	$3.89 \times 10^{-7}$	2.7	$3.66 \times 10^{-6}$
	$<3.5 \times 10^{-7}$	$<1.2 \times 10^{-7}$		
	$<3.5 \times 10^{-7}$	$<1.2 \times 10^{-7}$		
1.15	$9.00 \times 10^{-7}$	$2.63 \times 10^{-7}$	3.4	$2.84 \times 10^{-6}$
	$1.09 \times 10^{-6}$	$2.62 \times 10^{-7}$	4.2	$3.22 \times 10^{-6}$
	$8.58 \times 10^{-7}$	$3.12 \times 10^{-7}$	2.8	$2.96 \times 10^{-6}$
	$1.31 \times 10^{-6}$	$4.40 \times 10^{-7}$	3.0	$4.38 \times 10^{-6}$
1.25	$1.64 \times 10^{-6}$	$3.40 \times 10^{-7}$	4.8	$4.64 \times 10^{-6}$
	$1.67 \times 10^{-6}$	$4.20 \times 10^{-7}$	4.0	$5.02 \times 10^{-6}$
	$1.80 \times 10^{-6}$	$3.31 \times 10^{-7}$	5.4	$4.92 \times 10^{-6}$
1.35	$1.52 \times 10^{-6}$	$3.56 \times 10^{-7}$	4.3	$4.46 \times 10^{-6}$
	$1.66 \times 10^{-6}$	$4.59 \times 10^{-7}$	3.6	$5.16 \times 10^{-6}$
	$2.67 \times 10^{-6}$	$8.12 \times 10^{-7}$	3.3	$8.58 \times 10^{-6}$
	$2.84 \times 10^{-6}$	$7.22 \times 10^{-7}$	3.9	$8.56 \times 10^{-6}$
	$1.59 \times 10^{-6}$	$5.90 \times 10^{-7}$	2.7	$5.54 \times 10^{-6}$
	$2.32 \times 10^{-6}$	$9.44 \times 10^{-7}$	2.5	$8.40 \times 10^{-6}$
1.40	$2.34 \times 10^{-6}$	$9.00 \times 10^{-7}$	2.6	$8.28 \times 10^{-6}$
	$2.34 \times 10^{-6}$	$6.51 \times 10^{-7}$	3.6	$7.28 \times 10^{-6}$
	$2.11 \times 10^{-6}$	$6.96 \times 10^{-7}$	3.0	$7.02 \times 10^{-6}$

TABLE 8.--Continued

1.45	$2.79 \times 10^{-6}$	$7.77 \times 10^{-7}$	3.6	$8.69 \times 10^{-6}$
	$2.92 \times 10^{-6}$	$8.61 \times 10^{-7}$	3.4	$9.28 \times 10^{-6}$
	$1.42 \times 10^{-6}$	$5.89 \times 10^{-7}$	2.4	$5.20 \times 10^{-6}$
	$2.59 \times 10^{-6}$	$8.26 \times 10^{-7}$	3.1	$8.48 \times 10^{-6}$
1.55	$2.44 \times 10^{-6}$	$7.55 \times 10^{-7}$	3.2	$7.90 \times 10^{-6}$
	$2.73 \times 10^{-6}$	$9.25 \times 10^{-7}$	3.0	$9.16 \times 10^{-6}$
	$2.90 \times 10^{-6}$	$1.11 \times 10^{-6}$	2.6	$1.02 \times 10^{-5}$
	$2.47 \times 10^{-6}$	$9.70 \times 10^{-7}$	2.5	$8.82 \times 10^{-6}$
1.65	$3.03 \times 10^{-6}$	$5.14 \times 10^{-7}$	5.9	$8.12 \times 10^{-6}$
	$2.82 \times 10^{-6}$	$7.34 \times 10^{-7}$	3.8	$8.58 \times 10^{-6}$
	$2.43 \times 10^{-6}$	$8.12 \times 10^{-7}$	3.0	$8.11 \times 10^{-6}$
	$2.77 \times 10^{-6}$	$1.02 \times 10^{-6}$	2.7	$9.62 \times 10^{-6}$
1.75	$3.37 \times 10^{-6}$	$1.33 \times 10^{-6}$	2.5	$1.21 \times 10^{-5}$
	$2.80 \times 10^{-6}$	$1.06 \times 10^{-6}$	2.6	$9.84 \times 10^{-6}$
	$2.97 \times 10^{-6}$	$1.44 \times 10^{-6}$	2.1	$1.17 \times 10^{-5}$
1.85	$3.45 \times 10^{-6}$	$1.01 \times 10^{-6}$	3.4	$1.09 \times 10^{-5}$
	$3.94 \times 10^{-6}$	$1.52 \times 10^{-6}$	2.6	$1.40 \times 10^{-5}$
	$3.25 \times 10^{-6}$	$1.22 \times 10^{-6}$	2.7	$1.14 \times 10^{-5}$
1.95	$4.11 \times 10^{-6}$	$1.91 \times 10^{-6}$	2.2	$1.59 \times 10^{-5}$
	$3.53 \times 10^{-6}$	$1.60 \times 10^{-6}$	2.2	$1.35 \times 10^{-5}$
	$3.39 \times 10^{-6}$	$1.31 \times 10^{-6}$	2.6	$1.20 \times 10^{-5}$

TABLE 8.--Continued

2.05	$4.29 \times 10^{-6}$	$1.43 \times 10^{-6}$	3.0	$1.43 \times 10^{-5}$
	$4.31 \times 10^{-6}$	$1.74 \times 10^{-6}$	2.5	$1.56 \times 10^{-5}$
	$2.80 \times 10^{-6}$	$2.14 \times 10^{-6}$	1.3	$1.42 \times 10^{-5}$
2.15	$4.91 \times 10^{-6}$	$1.73 \times 10^{-6}$	2.8	$1.67 \times 10^{-5}$
	$4.09 \times 10^{-6}$	$1.97 \times 10^{-6}$	2.1	$1.61 \times 10^{-5}$
	$4.78 \times 10^{-6}$	$1.75 \times 10^{-6}$	2.7	$1.66 \times 10^{-5}$
	$4.50 \times 10^{-6}$	$1.68 \times 10^{-6}$	2.7	$1.57 \times 10^{-5}$
2.25	$4.52 \times 10^{-6}$	$1.74 \times 10^{-6}$	2.6	$1.60 \times 10^{-5}$
	$3.07 \times 10^{-6}$	$1.65 \times 10^{-6}$	1.9	$1.27 \times 10^{-5}$
	$6.28 \times 10^{-6}$	$2.13 \times 10^{-6}$	2.9	$2.11 \times 10^{-5}$
	$4.04 \times 10^{-6}$	$1.87 \times 10^{-6}$	2.2	$1.56 \times 10^{-5}$
	$4.16 \times 10^{-6}$	$1.77 \times 10^{-6}$	2.4	$1.54 \times 10^{-5}$
2.35	$4.56 \times 10^{-6}$	$1.89 \times 10^{-6}$	2.4	$1.67 \times 10^{-5}$
	$4.91 \times 10^{-6}$	$1.90 \times 10^{-6}$	2.5	$1.74 \times 10^{-5}$
	$4.50 \times 10^{-6}$	$1.91 \times 10^{-6}$	2.4	$1.66 \times 10^{-5}$

a. Platinum electrode anodized for 30 sec in 0.5 F sulfuric acid, chemical dissolution in 1 F hydrochloric acid at 85-95° for one hour.

b. A solution with an<sub>7</sub> absorbance of 0.030 at both 230 nm and 262 nm would contain  $3.5 \times 10^{-7}$  F of Pt(II) and  $1.2 \times 10^{-7}$  F of Pt(IV).

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