

Investigations of the Kinetics of Hydrogen and Oxygen Reactions on a Platinum Electrode in Acid Solution Using Pulse and Decay Techniques

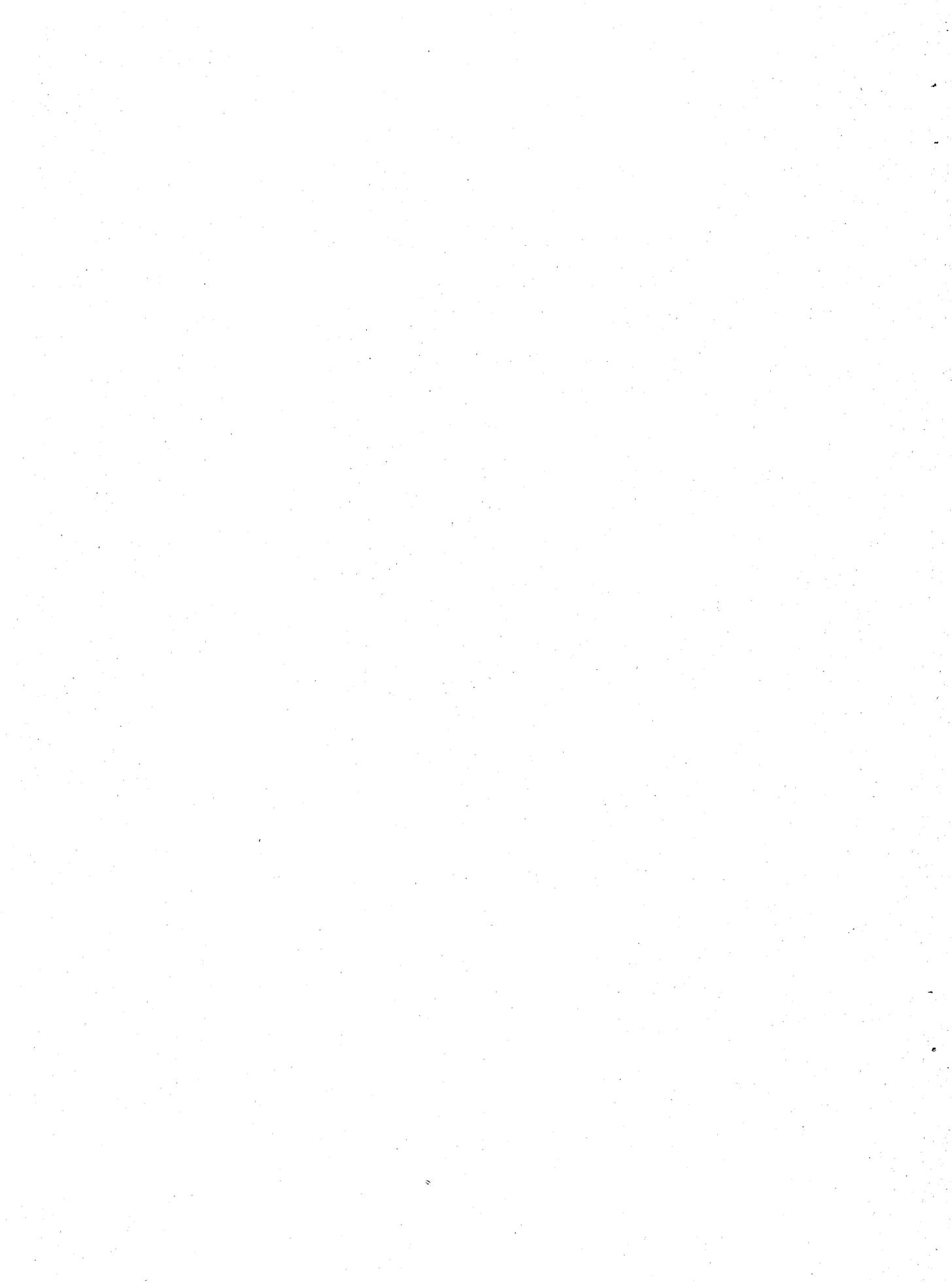
S. SCHULDINER AND T. B. WARNER

*Electrochemistry Branch
Chemistry Division*

September 4, 1964



U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.



CONTENTS

Abstract	iii
Problem Status	iii
Authorization	iii
DEFINITION OF SYMBOLS	iv
INTRODUCTION	1
EXPERIMENTAL	3
ANODIC CHARGING REACTIONS	4
CHEMICAL REACTION OF MOLECULAR HYDROGEN WITH CHEMISORBED OXYGEN ATOMS	9
ACKNOWLEDGMENTS	13
REFERENCES	13



ABSTRACT

The influence of hydrogen partial pressure, current density, and temperature on the anodic oxidation of sorbed H and the anodic generation of sorbed O were determined. Electrode processes were evaluated and separated to give the following quantities: (a) the amount of H associated with a Pt surface and its immediate vicinity, (b) the extent to reaction of H atoms, absorbed in the metal interior, that migrate to the surface of the metal and are either ionized or react with O atoms, (c) the extent of reaction of H₂ from the solution phase, (d) the amount of O adsorbed on the Pt surface, and (e) the amount of O absorbed in the Pt surface layers (skin).

The kinetics of the open-circuit reaction of galvanostatically determined amounts of sorbed O with H₂ were determined. This investigation showed that absorbed H and O in Pt significantly affect coulometric measurements at pulse lengths longer than about 1000 μ sec. The presence of absorbed O in the Pt can also materially affect the reaction rate of chemisorbed O with H₂. Under the experimental conditions transport of reactants on the solution side was fast enough so that diffusion did not limit processes in either the H ionization or O sorption regions. The data indicated that migration of adsorbed species on the Pt surface to active sites was rate controlling in the O sorption region, except in the case of reaction of adsorbed O with H₂ when significant amounts of O were adsorbed in the skin of the Pt. In this case the chemical reaction rate between adsorbed O and H₂ was retarded so that this chemical step appeared to be rate determining. Reaction rates of the adsorbed O and H₂ reaction under open-circuit conditions were determined at varying temperatures, adsorbed and absorbed O concentrations, and H₂ partial pressures.

PROBLEM STATUS

This is an interim report on one phase of the problem of electrode mechanisms; additional work on this problem is continuing.

AUTHORIZATION

NRL Problems C05-06 and C05-13
Projects SR 007-12-01-0809 and RR 001-01-43-4754

Manuscript submitted June 22, 1964.

DEFINITION OF SYMBOLS

(Fig. 1a delineates and defines the major reaction regions and potentials in the charge and decay traces.)

- H_s - hydrogen atoms associated with Pt atoms on the surface and immediately below the surface. Operationally, H_s is the time-independent amount of H atoms coulometrically measured with an anodic pulse that polarizes the electrode through the H ionization region in less than 1000 μsec . At a Pt electrode under 1 atm H_2 at 25°C, $H_s = 230 \mu\text{coul}/\text{cm}^2$.
- H_i - hydrogen atoms located in the interior of a Pt electrode. Operationally, these H atoms do not migrate to the surface and react under the conditions referred to under H_s . H_i atoms only add to the measured number of coulombs at polarization times longer than 1000 μsec .
- H_2 - molecular hydrogen in the solution phase.
- i_r - number of $\mu\text{coul}/\text{cm}^2$ of O generated during an anodic pulse divided by the time, in μsec , required to reduce this O with H_2 plus H_i which migrates to the surface.
- O_{ad} - oxygen atoms chemisorbed on the Pt electrode surface. By the definition of area used, these atoms are in a one-to-one correspondence with surface Pt atoms. Operationally, O_{ad} is the time-independent amount of O atoms coulometrically measured with an anodic pulse that polarizes the electrode through the O sorption region in less than 1000 μsec . At 25°C, $O_{ad} = 420 \mu\text{coul}/\text{cm}^2$.
- O_{ab} - oxygen atoms absorbed in the skin of the Pt electrode. Operationally, these atoms only add to the measured number of coulombs at polarization times longer than 1000 μsec .
- q_H - the number of $\mu\text{coul}/\text{cm}^2$ of reaction in the H ionization region.
- q_O - the number of $\mu\text{coul}/\text{cm}^2$ of reaction in the O sorption region.
- $q_{H,ex}$ - the number of $\mu\text{coul}/\text{cm}^2$ of hydrogen oxidized in the H ionization region in excess of the amount of hydrogen atoms (H_s) originally associated with the electrode surface before imposition of the anodic pulse. $q_{H,ex}$ is due to oxidation of H_i and H_2 .
- $q_{O,ex}$ - the number of $\mu\text{coul}/\text{cm}^2$ of charge expended in the O sorption region in excess of the amount required to generate the O atoms (O_{ad}) chemisorbed on the Pt surface. $q_{O,ex}$ is due to the formation of O_{ab} and of the oxidation of H_i and H_2 .
- θ - fraction of available sites on the surface covered.

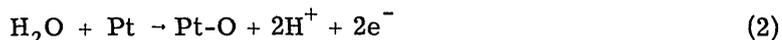
INVESTIGATIONS OF THE KINETICS OF HYDROGEN AND OXYGEN
REACTIONS ON A PLATINUM ELECTRODE IN ACID SOLUTION
USING PULSE AND DECAY TECHNIQUES

INTRODUCTION

This investigation was carried out to determine the influence of hydrogen partial pressure, current density, and temperature on (a) the anodic oxidation of adsorbed hydrogen



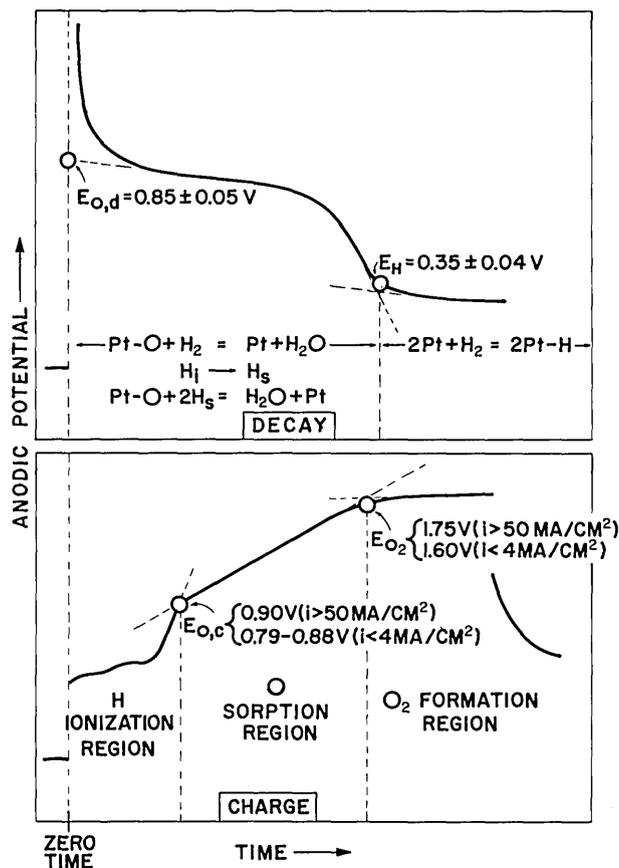
where Pt- indicates a chemisorbed species, and (b) the anodic generation of atomic oxygen



on a platinum electrode. By use of relatively fast (i.e., high current density) constant current anodic pulses, only that hydrogen already sorbed on the Pt electrode is ionized, and a given number of O atoms are generated and adsorbed on the electrode surface without a significant number of these O atoms absorbing into the outermost layers (skin) of Pt (1-3), or combining to O₂ and diffusing away into solution. By use of longer charging times (i.e., low current densities), some H₂ in solution is ionized in addition to the originally sorbed hydrogen, and a large part of the deposited O atoms is absorbed into the surface layers of Pt during the time of the applied pulse and more than a monolayer is deposited. Previous work at this Laboratory (1,3), as well as the work of others, has indicated that O atoms formed during anodic polarization in the O sorption region primarily will either be chemisorbed on the Pt electrode surface or be absorbed in the surface layers of the Pt electrode. In addition, if H atoms are dissolved in the Pt bulk, they may migrate to the surface and either be ionized or react with O atoms.

It has been shown (1,4) that the rate of reaction of molecular hydrogen in solution with chemisorbed O atoms at potentials above 0.9v (vs N.H.E.) is relatively slow; hence low-current-density charging pulses were used to determine the combined amount of adsorbed and absorbed O and the reaction of adsorbed O with H₂. The amount of reaction involving H₂ can be determined by comparing such curves with charging curves obtained in hydrogen-free solution. The amount of H_i which migrates to the surface where it is oxidized can be determined in H₂-free solutions by subtracting the number of coulombs required to charge a Pt electrode, free of H_i, to the O₂ evolution potential from the number of coulombs required to charge the same Pt electrode containing H_i over the same potential range. Thus, the amount of fast-reacting sorbed hydrogen, H_s, the additional hydrogen reacting from solution, H₂, and from the metal interior, H_i, the amount of O atoms adsorbed on the Pt surface, O_{ad}, the amount of O atoms absorbed into the skin of the Pt, O_{ab}, and the amount of reaction of H₂ with adsorbed O atoms can all be determined using the operational definitions of these quantities.

Experiments were conducted to determine the kinetics of the reaction of O_{ad} with H₂ under open-circuit conditions. Here the electrode was coulometrically charged (see Fig. 1b) with a known amount of O_{ad} or O_{ad} plus O_{ab} and the pulse terminated. The potential



(a) Oscilloscope traces. Delineation and definition of the major reaction regions and potentials in charge and decay traces.

(b) Oscilloscope traces. Typical anodic charging curves ($50 \mu\text{sec}$ per horizontal division, 0.5v per vertical division, $i = 2.61 \text{ amp/cm}^2$) and decay curves ($2000 \mu\text{sec}$ per horizontal division, 0.2v per vertical division) at 50°C and $p_{\text{H}_2} = 0.88 \text{ atm}$.

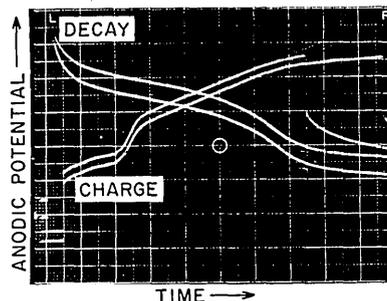


Fig. 1 - Oscilloscope traces

decay with time was then photographically recorded from an oscilloscope trace (see Fig. 1b) from which the time for reaction of O_{ad} with H_2 in solution plus H_i which migrates to the surface could be measured.

Breiter (5) also used a kinetic technique involving the reduction of chemisorbed oxygen with H_2 . However, the method used in this report varies in several important respects from that of Breiter. In our work we can distinguish between O chemisorbed on the electrode surface and that absorbed into the skin of the metal. Breiter's potentiostatic method (5) undoubtedly included both O_{ad} and O_{ab} . In this report we shall show that the presence of O_{ab} can materially affect the rate of the reduction of O_{ad} with H_2 . Breiter (5) determined the amount of sorbed O at a given anodic potential by using a cathodic

sweep which did not clearly separate the oxygen region from the double layer region. In our work we form a given amount of O with an anodic charging pulse where we can separate the amount of O_{ad} present from the amount of O_{ab} dissolved in the Pt electrode. We can also correct for the double layer charge (1). The significance of Breiter's determination of reaction rates at given decay potentials is difficult to assess since his electrode probably contained both O_{ad} and O_{ab} . His reaction rates for different polarization potentials decreased with increased polarization potential, and since potentiostatic charging for 60 sec is adequate time for considerable absorption of O, his decrease in reaction rate can be explained by increased amounts of O_{ab} at higher polarizing potentials.

Our method does suffer in that it does not determine reaction rate as a function of decay potential, but yields the integrated reaction rate over the entire decay potential range. We can, however, limit the potential to which the electrode is anodically charged and thereby successively decrease the amount of O formed. This permits us to show the effects of reduced surface coverage of O on its reaction rate with H_2 .

EXPERIMENTAL

The electrochemical system, gas purification trains, and general procedures have been described elsewhere (1-3). True areas (about 0.3 cm^2) of the working Pt bead electrode were defined using the method previously reported (1,6), and cleanliness of the working electrode and solution was verified by the configuration of the anodic charging curve in the O sorption region (6). The electrolyte was 1M sulfuric acid solution and was maintained at a constant temperature ($\pm 0.5^\circ\text{C}$) with a water bath. Water bubblers used to saturate the helium or hydrogen going into the cell were kept in the same constant temperature bath to maintain the same partial pressure of water vapor and thereby to keep the electrolyte concentration in the cell constant.

After pre-electrolysis of the solution, the temperature of the water bath was set at a given value and an appropriate mixture of hydrogen and helium (or one of these pure gases) was bubbled through the cell at given rates (0 to 1300 ml/min) as determined with one or two flowmeters. Zero stirring rate measurements were taken shortly after stopping the flow of a given gas or gas mixture into the cell. The electrometer, pulse generator, and oscilloscope used were the same as previously reported (3), as were the reference (Pt wire and miniature glass) and counter (Pd tube) electrodes. In order to polarize the Pt bead electrode up to the O_2 region with low-current-density pulses ($< 5 \text{ ma/cm}^2$), long-duration pulses ($> 0.5 \text{ sec}$) were required. These pulses were generated with an Electronic Measurements Solid State (Model C612) Constant Current power supply, using a telegraph key to switch the current on and off. The resulting charging curves were photographed from the oscilloscope screen.

Single-shot, constant-current pulses were used to determine the anodic charging curves. After a current pulse, the electrode was permitted to recover to its normal open-circuit potential before the next pulse was applied. Pulse current densities were varied from $780 \text{ } \mu\text{a/cm}^2$ to about 3 amp/cm^2 . The $\mu\text{coul/cm}^2$ of hydrogen ionized and oxygen formed were corrected for double layer charging by using a previously determined relationship between double layer capacitance and potential (1).

After anodic charging curves were taken under a variety of conditions, a series of photographs were made showing the polarization decay in H_2 -saturated solution (varying H_2 partial pressures and temperatures) at the Pt bead electrode, which was previously charged with a known number of coulombs to a given potential in the O sorption region or somewhat beyond in the O_2 formation region. (Figure 1a delineates the various regions for the charging and decay traces.) In these experiments a charging pulse was set for a given duration and an oscillogram taken (see top charge curve in Fig. 1b). The oscilloscope sweep rate was then considerably slowed and the voltage amplification increased

so that the pulse itself was largely off the screen and lasted only a very small fraction of the total time displayed. Then the decay curve (see decay curves in Fig. 1b) following pulse cutoff ran for the length of the horizontal sweep until the potential and shape of the decay curve showed complete removal of sorbed oxygen. Thus, with this technique a known number of O atoms could be formed on the surface and the time required for their subsequent open-circuit reaction with molecular hydrogen in solution determined.

ANODIC CHARGING REACTIONS

From the photographed anodic charging traces (Fig. 1b), the number of $\mu\text{coul}/\text{cm}^2$ of both ionized H and O formed on the Pt bead electrode was determined. These values were corrected for double layer charge. For high-current-density anodic pulses (1 to 3 amp/cm²) only O_{ad} is formed, and the number of coulombs used to charge the O sorption region at room temperature was used to define the surface area (1) of the Pt bead. Under these conditions the O sorption region was assumed to require 420 $\mu\text{coul}/\text{cm}^2$ to charge (equivalent to one monolayer, one-to-one correspondence with surface Pt atoms); the H ionization region was found to require 230 $\mu\text{coul}/\text{cm}^2$ to charge. The 230 $\mu\text{coul}/\text{cm}^2$ of H oxidized represents the amount of H (H_s) associated with the Pt surface under open-circuit conditions ($p_{\text{H}_2} = 1$ atm). Experimental evidence (1,7) indicates that part of this hydrogen is chemisorbed on the Pt surface as atoms and part is absorbed primarily in the outermost layers of the Pt. The experimental data at 23°C showed that within experimental error, this quantity of H, for the higher current density pulses, was virtually independent of the hydrogen partial pressure in the cell (0.02 to 1 atm). This indicated that the amount of chemisorbed hydrogen in rapid equilibrium with H₂ gas above the solution is very small at room temperature and verifies previous work from this Laboratory (1,8).

At lower current densities, the amounts of charge consumed in both the H and the O regions exceeded 230 and 420 $\mu\text{coul}/\text{cm}^2$, respectively. These excesses of charge, q_{ex} , represented: (a) the amount of hydrogen in the H ionization region, $q_{\text{H,ex}}$, oxidized beyond the amount of hydrogen, H_s, originally associated with the surface before imposition of the anodic pulse, and (b) the excess charge in the O sorption region, $q_{\text{O,ex}}$, which was due primarily to the oxygen, O_{ab}, formed beyond that needed to form a single monolayer of O atoms, O_{ad}, plus any H₂ and H_i oxidized.

Figure 2 shows both the current density and the hydrogen partial pressure effects on $q_{\text{H,ex}}$ and $q_{\text{O,ex}}$. The $q_{\text{H,ex}}$ can come from two sources, the molecular hydrogen, H₂, bubbled into the cell and the hydrogen dissolved in the interior, H_i, of the Pt bead diffusing out to the surface. Estimations of the amount of H_i which diffused to the surface and then was oxidized were made in pure helium-saturated solutions (the electrode was first saturated with H₂, $p_{\text{H}_2} = 1$ atm, then the H₂ was replaced with He and charging curves were obtained). These experiments showed that with current density pulses of higher than 0.203 amp/cm², virtually no hydrogen diffused from the interior of the Pt bead to the surface during the charging pulse. At lower current densities, some hydrogen coming from this source was detected and the $p_{\text{H}_2} = 0$ points in Fig. 2a roughly indicate their values. Interestingly, the amount of H_i (about 300 $\mu\text{coul}/\text{cm}^2$) diffusing to the surface at current densities of 3.53 ma/cm² and lower was essentially independent of current density.

The $q_{\text{O,ex}}$ appears to represent primarily the amount of O_{ab} in the skin of the Pt bead plus the possible reaction of H₂ and the H_i which diffused to the surface during anodic charging. Lack of stirring effects made it unlikely that a significant amount of oxygen was lost from the surface in the form of O₂ in the O sorption region. Reaction of O_{ad} with H₂ at potentials in the O sorption region has been shown to be slow (1,4); however, the data in Fig. 2b show that at current densities of 3.5 ma/cm² and lower, a significant amount of reaction of O_{ad} with H₂ must occur. This is because both stirring and increased hydrogen partial pressure cause an increase in the amount of charge

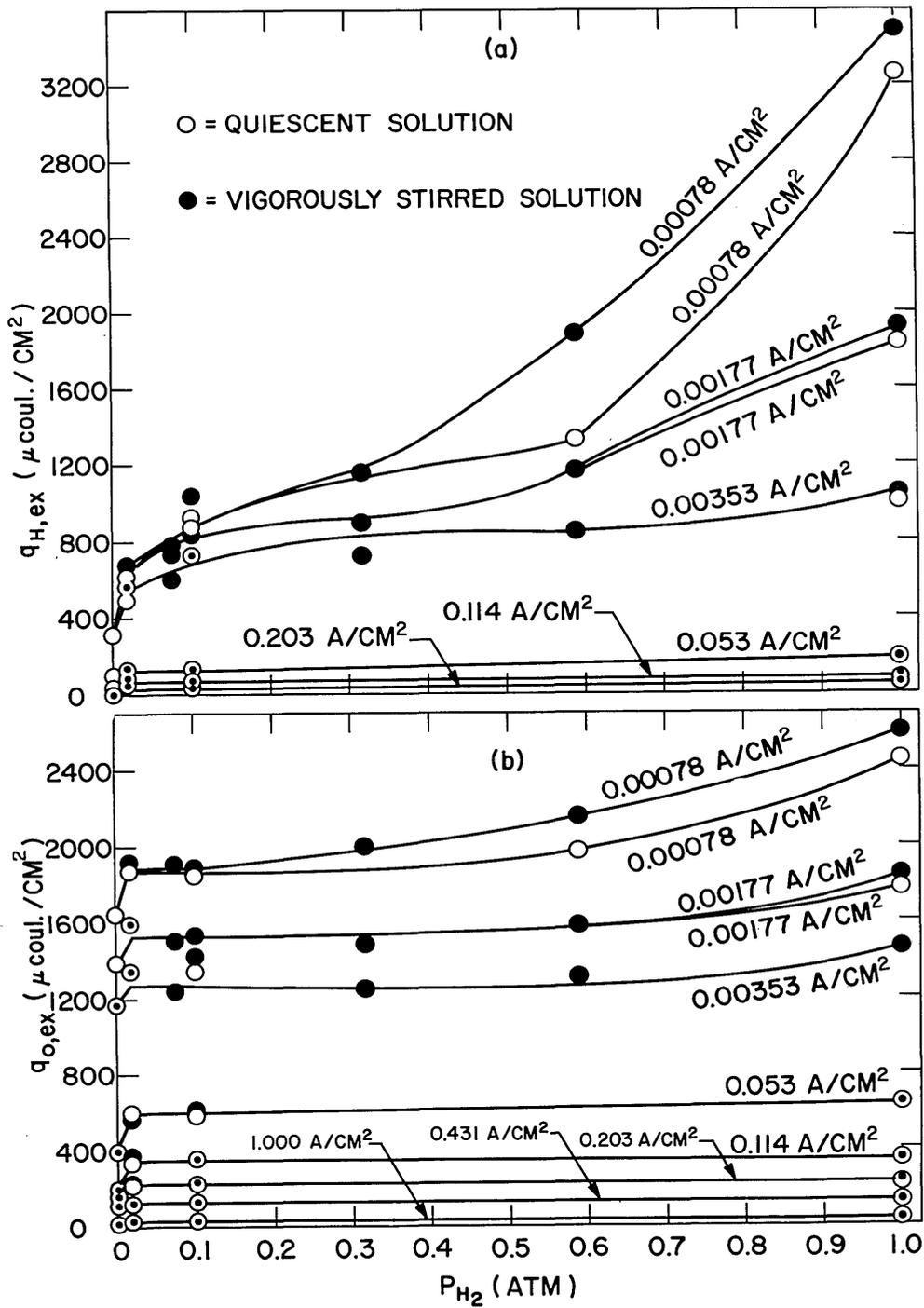


Fig. 2 - Data from anodic charging curves at 23°C. Effects of current density, stirring, and hydrogen partial pressure on excess of charge in (a) the H ionization region, $q_{H,ex}$, and (b) the O sorption region, $q_{O,ex}$.

consumed in the O sorption region. However, as the hydrogen partial pressure is decreased, eventually the number of coulombs of charge transferred does not vary even with stirring. But even at these low hydrogen partial pressures there evidently is some reaction of O_{ad} with H_2 , because when the hydrogen partial pressure is reduced to zero, the amount of charge expended decreases. In fact, even at current densities as high as 0.203 amp/cm^2 there appears to be a significant amount of reaction of O with H_2 . The fact that there are conditions under which hydrogen partial pressure and/or increased stirring does not affect the apparent amount of hydrogen reaction with O_{ad} means that under these conditions the transport of H_2 to the electrode surface by convection and diffusion is faster than the reaction of H_2 with O_{ad} .

At the lowest current density pulse applied (0.78 ma/cm^2), increased stirring rates above those used in the Fig. 2a data considerably lengthened the hydrogen ionization region on the oscilloscope trace. With a small decrease in current it was impossible to polarize the electrode beyond the hydrogen region. This showed that the exchange current density, i_0 , for the hydrogen reaction is close to 0.78 ma/cm^2 and that extremely fast stirring is necessary to minimize diffusion polarization. This value checks previous steady-state measurements (9) from this Laboratory when the previous values are adjusted to correspond to the definition of true surface area used here. On the other hand, the length of the O_{ad} region was virtually independent of further increases in the hydrogen stirring rate, beyond the corresponding values shown in Fig. 2b, at 0.78 ma/cm^2 . This demonstrated the i_0 , for the reaction of H_2 with O_{ad} , is considerably less than 0.78 ma/cm^2 , and it also follows that diffusion polarization of H_2 in the vigorously stirred solution was insignificant.

The data shown in Fig. 2b for the helium-stirred solution ($p_{H_2} = 0$, Pt electrode containing H_i) gives the sum of H_i atoms which diffuse to the surface and are ionized and of O_{ab} generated during the anodic pulse. At the lowest current density this amounts to the equivalent of about four atomic layers of O.

Experiments conducted in helium-saturated solution in which H_i in the Pt bead was completely removed (potential vs N.H.E. was 0.47 to 0.59 v), showed that the amount of O_{ab} in the skin of the metal was 910, 1020, and $1260 \mu\text{coul/cm}^2$ at current densities of 3.53, 1.77, and 0.78 ma/cm^2 , respectively. The $p_{H_2} = 0$, values shown in Fig. 2b, for the same series of current densities, include oxidized H_i and O_{ab} and are 1170, 1400, and $1630 \mu\text{coul/cm}^2$, respectively. The amount of H_i which diffuses to the surface and is oxidized appears to level off at about $400 \mu\text{coul/cm}^2$ at the two lowest current densities, but at all these low current densities the H_i contribution is significant.

The $p_{H_2} = 0$ values shown in Fig. 2b therefore account for both oxidized H_i and O_{ab} and the difference between $q_{O,ex}$ values at $p_{H_2} > 0$ and $p_{H_2} = 0$ represents the amount of H_2 from solution which is ionized. The high $q_{O,ex}$ values for the low-current density data indicate that the top layers of Pt atoms in the metal skin may be fairly well saturated with oxygen. As will be shown later this can have a marked effect on the catalytic behavior of Pt.

The data in Fig. 2 show large differences in $q_{H,ex}$ and $q_{O,ex}$ for given current density pulses. Using these curves the amount of H_2 ionized in the H-ionization region and H_2 reacting in the O sorption region were separated from the total q_{ex} values and compared. This comparison showed that at current densities of 3.53 ma/cm^2 and lower, the number of equivalents of H_2 reacting in the O sorption region is considerably less than the number of equivalents of H_2 being ionized in the hydrogen region, even though the duration of the O sorption region is about twice as long. At current densities of 0.053 amp/cm^2 and higher the reverse occurs; here considerably more H_2 reacts per unit time in the O sorption region than in the H ionization region. These experimental facts show (a) that hydrogen diffusion cannot be rate controlling in both the H ionization and O sorption regions, otherwise the number of coulombs of H_2 per unit time reacting in both

regions would be identical, (b) at low-current densities, H_2 is ionized much faster in the H ionization region than H_2 reacts with O_{ad} in the O sorption region, therefore, H_2 diffusion cannot be rate controlling in the O sorption region, and (c) at the higher current densities, H_2 reacts with O_{ad} faster in the O sorption region than these molecules are ionized in the H ionization region; here one concludes that H_2 diffusion cannot be rate controlling in the H ionization region.

The exchange current densities of both the charge transfer and molecular dissociation steps of the hydrogen reaction have been shown (1,8,9) to be independent of the charging rate. Hence, the differences in the reaction rates of H_2 at the anodized Pt bead at low- and high-current densities must be in the O sorption region. We believe that the rate of reaction of H_2 with O_{ad} is faster with high-current density pulses because less O is absorbed into the skin of the Pt under these conditions. The work which will be reported in the last section of this paper will further verify that the rate of the reaction between H_2 and O_{ad} is strongly dependent on the amount of O_{ab} in the skin of the Pt electrode.

Temperature Effects - The effects of temperature on both the H ionization and O sorption regions are shown in Fig. 3. The curves in Fig. 3a for the H ionization region indicate that the effect of temperature is essentially the same for all current densities, the lower current density pulses showing additional discharge due to reaction of H_2 that comes from the solution. The fact that there is an inverse temperature effect seems to indicate that the lower H_2 partial pressure at higher temperatures would be an important factor. Nevertheless, the data in Fig. 2a clearly shows that at the current densities involved, the effect of H_2 partial pressure is essentially negligible at 23°C.

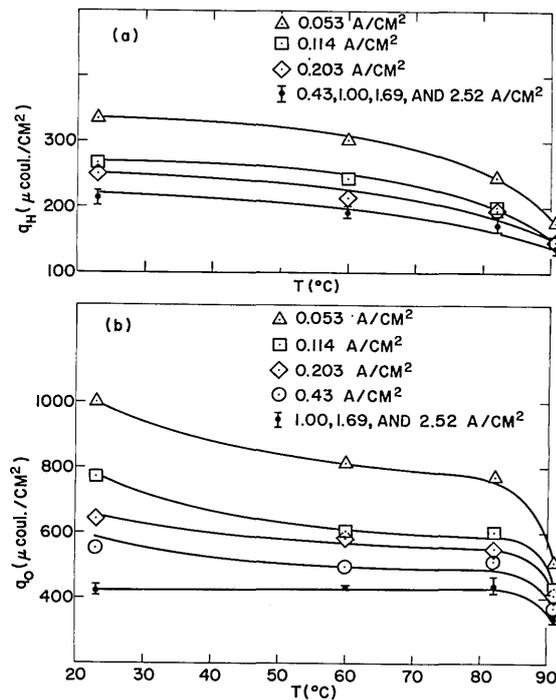


Fig. 3 - Temperature effects on anodic charging curves (a) q_H in hydrogen ionization region, (b) q_O in oxygen sorption region

One important factor brought out by these curves (Fig. 3a) is that the amount of H_s decreases as the temperature increases. This can be seen especially for the high-current density curve where the ionization of extra H_2 from solution would be unimportant. This decrease in the amount of H_s could be due essentially to the lower H_2 partial pressure at higher temperatures. Thus, even though the 23°C case apparently shows independence of the amount of H_s with p_{H_2} , this may be due to the fact that at this temperature the equilibrium between H_s and H_2 may take a relatively long time to be established.

It could well be that the loss of the bulk of the hydrogen from Pt is not through equilibration with H_2 dissolved in the solution, but is due to reaction with trace amounts of oxygen which leak into the system. Thus steady-state potentials of such a Pt/H electrode at values less than about 0.3 v vs N.H.E. may be owing to an equilibrium



A similar equilibrium has been postulated for α Pd-H (10). At higher temperatures, however, changes in the amount of H_s may occur more rapidly and H_s (and H_i) is less at increased temperatures because of reduced H_2 partial pressures.

Because the curves in Fig. 3a are essentially parallel, the effect of temperature on $q_{H,ex}$ can be considered to be constant. Unfortunately, it is not possible with this data to separate H_2 partial pressure from temperature effects. Measurements were taken in both quiescent and stirred solution (zero and 1300 ml/min gas flow, respectively). Under both conditions, the numbers of coulombs measured for the data (except at the lowest current densities) shown in Fig. 2a were essentially the same. Where there is no stirring effect, we are led to believe that diffusion of H_2 from the solution was not the controlling factor. Hence, we conclude that the rate-controlling step for the ionization of the molecular hydrogen which comes from solution is the dissociation of H_2 to H.

Temperature effects (Fig. 3) in the O sorption region are quite different from those in the H ionization region. Figure 3b shows that at high-current densities, where only surface adsorption of O occurs, q_o is independent of temperature with the exception of the 91°C value. The temperature invariance indicates that a transport or charge transfer step may be rate controlling. Here also diffusion in solution can be ruled out by the lack of stirring effects. The transport here most likely involves either the migration of a water molecule to a site where it can be oxidized or the migration of an O atom to a suitable site on the electrode surface. The sudden drop in q_o at 91°C is difficult to explain. There are several possibilities: (a) the effects of electrode poisons would most likely increase at higher temperatures and the reproducibility of the data being poorest at this temperature would tend to support this, and (b) the bonding of O_{ad} at 91°C may be such that a linear bond with surface Pt atoms no longer predominates and therefore full coverage would be less than 420 μ coul/cm². Our cleanliness tests at 91°C and after immediate lowering of temperature did not indicate impurity adsorption; however, we cannot be sure that some self-poisoning process did not occur at this temperature.

The lower current density (0.053 to 0.43 amp/cm²) data in Fig. 3b show a definite temperature effect of $q_{O,ex}$ throughout the entire temperature range. The curves are roughly parallel and here again diffusion control in solution is unlikely due to the absence of stirring effects. The fact that there is an inverse temperature effect may be due to a decrease in the solubility of O in the metal skin as the temperature increases and thereby the rate of absorption which gives $q_{O,ex}$ decreases. Decreased hydrogen partial pressure is probably also a factor.

These temperature effects indicate that important changes are taking place, not only on the surface but in the surface layers of the Pt electrode. More work is

contemplated on the absorption of O into the skin and the effects of these absorbed atoms on the surface reaction kinetics.

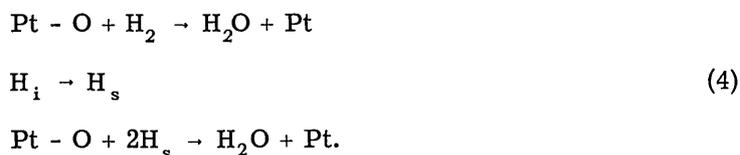
CHEMICAL REACTION OF MOLECULAR HYDROGEN WITH CHEMISORBED OXYGEN ATOMS

The unique feature of the technique used to study the reaction of H₂ with O_{ad} is that electrochemical measurements were used not only to determine the kinetics of a chemical reaction occurring on a metal surface under open-circuit conditions, but the effects of the various sorbed species could be isolated. Accurate control of the amount of O_{ad} was possible by coulometric means. Also, the effects of O_{ab} on the rate of the surface reaction between O_{ad} and H₂ could be determined.

The data in Fig. 4 give the reaction rate

$$i_r = \frac{\text{number of } \mu\text{ coul/cm}^2 \text{ of O generated during the anodic pulse}}{\mu\text{ sec required to reduce O with H}_2 + \text{H}_i \text{ which migrates to the surface}}$$

where i_r is expressed in amp/cm². The chemical reactions involved are



With the high-current densities (1.66 to 3.36 amp/cm²) used to collect the data shown in Fig. 4, absorption of O during anodic charging was found to be negligible. The data for $q_{\text{O}} > 420 \mu\text{ coul/cm}^2$, $E_{\text{O}_2} \approx 1.8 \text{ v}$, also indicates that an excess of adsorbed O can be formed in the O₂ formation region. These excess O atoms are evidently not lost by diffusion into solution as O₂ in the fast pulse times used. This may indicate that initially at E_{O₂} at least as much as about another monolayer of O atoms can be held on the electrode surface. These extra O atoms may easily go into the interstitial holes in the Pt lattice (especially in the 110 plane). The potential may simply be a function of the coverage of surface atoms with O_{ad}. After these surface atoms are saturated, the holes in the lattice are filled without apparently affecting the potential and, as the data in Fig. 4 show, the reaction rate, i_r , of Eq. (4) is independent of the surface coverage from one monolayer up to about two monolayers. It is also possible that the extra oxygen is in the molecular form and is held in position firmly enough so that losses are negligible during both the formation of oxygen and reaction with H₂. A third possibility is that PtO₂ is formed at E_{O₂} before the generation of O₂. Molecular hydrogen then reacts with both PtO₂ and Pt-O at essentially the same rate.

Blank runs were attempted at 23°C to estimate the effects of H_i migrating to the surface and reacting with O_{ad}. The electrode was first exposed in 1 atm H₂ saturated solution and then the H₂ was replaced with pure He. After sweeping out the solution with He for about 20 minutes, the potential became more anodic by about 60 mv. Decay traces in this solution (p_{H_2} calculated $< 0.01 \text{ atm}$) gave i_r values equal to a little over one-half of the i_r values found in H₂ swept solutions, except where q_{O} was less than about 200 $\mu\text{ coul/cm}^2$. As $q_{\text{O}} \rightarrow 0$, i_r approached the values shown in Fig. 4a, since even at $p_{\text{H}_2} < 0.01 \text{ atm}$, significant amounts of H₂ remained in solution. Unfortunately, an experiment to determine clearly the effect of H_i was not possible. The experiment shown in Fig. 2 indicated that H_i was equivalent to 300-400 $\mu\text{ coul/cm}^2$. Since the data in Fig. 4 shows that i_r was constant after approximately a monolayer of O_{ad} was removed, it indicates that the contribution of H_i, which is apparently not in excess of the equivalent of

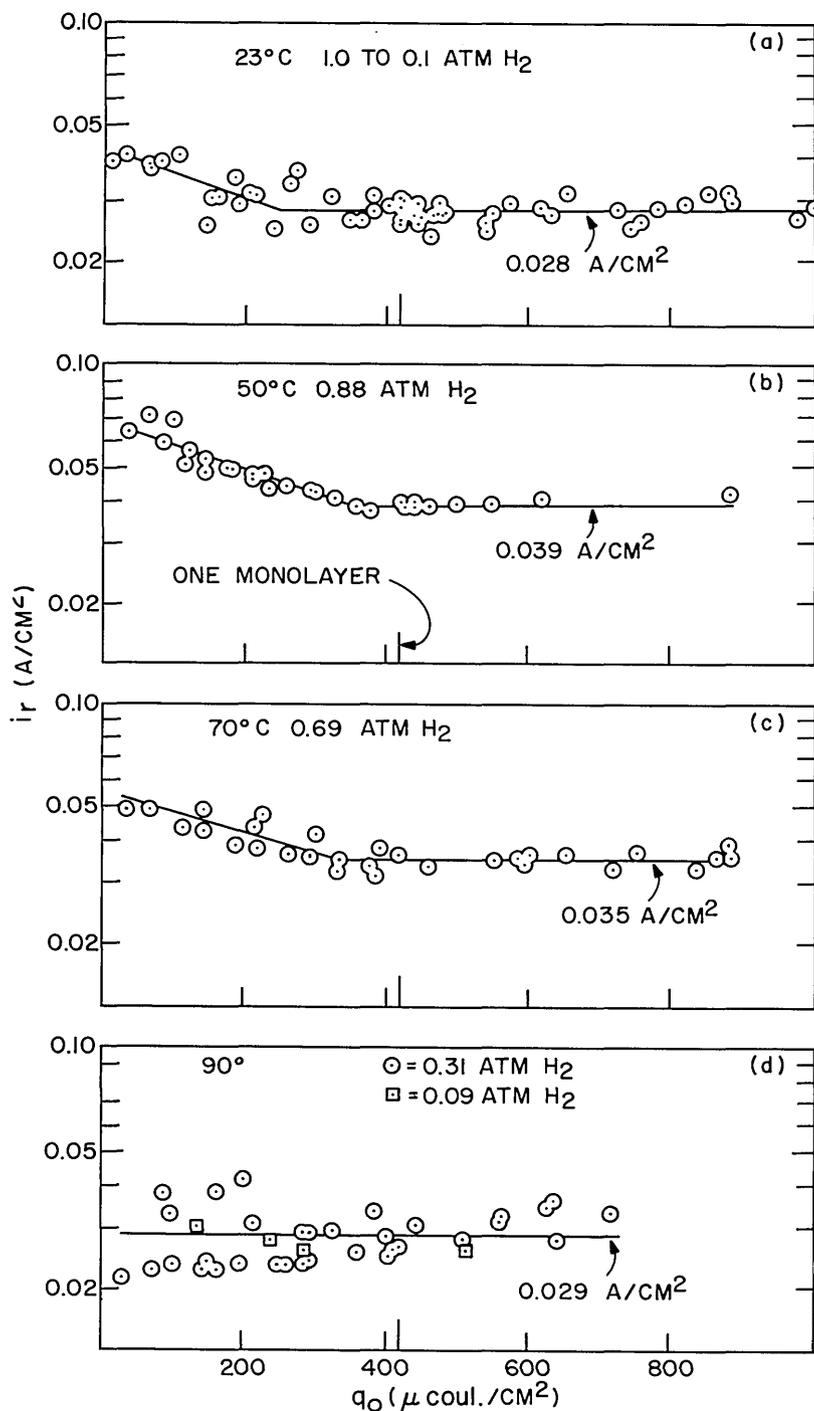


Fig. 4 - Rates of reaction, i_r , of O_{ad} with H_2 plus H_s obtained from decay curves following high-current density anodic pulses terminated at various points in the O sorption or O_2 formation regions (no O_{ab} generated)

one monolayer of O_{ad} , may only affect i_r at low coverages. In any case, the influence of H_i could not affect i_r by more than a factor of 2.

The values of i_r in the plateau regions of Fig. 4 can be considered to be essentially independent of both temperature and hydrogen partial pressure. (The data in Fig. 4a showed a random scatter of points at 0.1, 0.5, and 1 atm H_2 partial pressures.) The values shown in Fig. 4 were taken also at stirring rates beyond which i_r did not increase with increasing stirring. The lack of stirring rate and H_2 partial pressure effects eliminates the diffusion of H_2 from solution as the rate-controlling mechanism. The lack of H_2 partial pressure and temperature effects also eliminates the direct chemical reaction of H_2 with O_{ad} as a possible rate-determining step. A third possible controlling step is one which involves a dissociation of H_2 into atoms and its migration across the surface to active sites bearing O atoms where the reaction in Eq. (4) can occur. It is also possible that the rate-controlling step may be the migration of O_{ad} to the active sites where they can react with either atomic or molecular hydrogen.

The fact that i_r at $p_{H_2} = 1$ atm after subtracting the i_r at $p_{H_2} < 0.01$ atm gives values somewhat higher than 0.01 amp/cm², which is about one order of magnitude higher than i_r for the molecular hydrogen ionization reaction (0.00078 amp/cm² or 0.0016 amp/cm² on an apparent area basis), demonstrates that (a) diffusion of H_2 cannot be rate controlling in the H-ionization region because the reaction with H_2 shown in Eq. (4) occurs faster under equal stirring rates, and (b) H_2 does not dissociate into atoms before reacting with O_{ad} , because here again the reaction of O_{ad} with H_2 is faster than the ionization of H_2 which requires dissociation into atoms. Taking all of these facts into consideration, the most likely rate-controlling step for the reaction between H_2 and O_{ad} is the migration of O_{ad} atoms to active sites where they can directly react with H_2 .

At lower surface coverages, θ ($\theta < 1$), the data in Fig. 4 show that i_r increased as the surface coverage decreased. This suggested, since the most active sites would be covered with O_{ad} first, that the decrease in the number of inactive sites covered with O_{ad} reduced the amount of necessary migration to active sites and thereby i_r tended to increase. This argument also supports the O_{ad} migration step as the rate-controlling one.

When charging pulses from 0.053 to 1.0 amp/cm² were used to form the O sorption region, the rate of charging was slow enough so that some of the O atoms formed absorbed into the skin of the Pt bead and, possibly, some H_i atoms migrated to the surface (as shown in the previous section). Under these conditions, at the end of the charging pulse part of the O atoms formed were adsorbed on the Pt surface and part absorbed in the skin of the electrode. Loss due to reaction with H_i and with H_2 from solution during charging was significant mainly at current densities below 0.2 amp/cm², and even at the lower current densities used only a fraction of the O_{ad} reacted with H_i or H_2 (see Fig. 2b).

The data in Fig. 5 were obtained with pulses which were terminated just at the end of the O sorption region (see, for instance, upper charge curve in Fig. 1b), but which were of such low current density that additional amounts of oxygen could dissolve in the Pt. This is in contrast to the data in Fig. 4, which were obtained with high-current density pulses. Some of these latter pulses were long enough to charge well into the O_2 formation region, some were terminated just at the end of the O sorption region, and some were terminated at various points within the O sorption region.

Figure 5 shows the O_{ab} has a marked effect on i_r . The reaction current density, i_r , of Eq. (4) is sharply diminished as the amount of O_{ab} increases (correction of i_r for any reduction of O_{ad} due to migration of residual H_i to the surface during charging would tend to decrease i_r further). Figure 5a shows the i_r is a direct function of p_{H_2} . Determinations of i_r at $23^\circ C$ in $p_{H_2} < 0.01$ atm solution gave values slightly lower than for the 0.1 -atm- H_2 curve shown. This indicated that H_i was an important factor, at least in the $p_{H_2} < 0.01$ atm case. Figure 5b shows that although increased temperature tends to

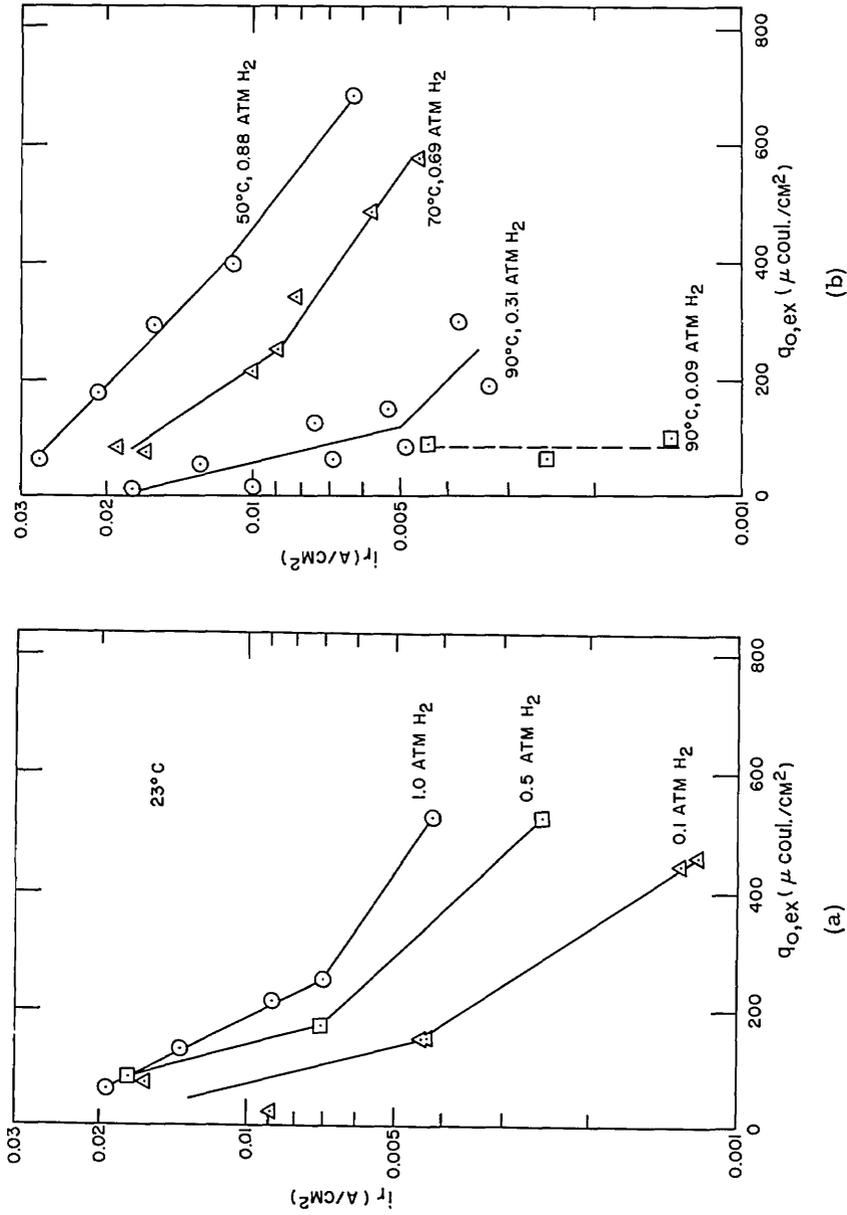


Fig. 5 - Rates of reaction, i_r , of O_{ad} with H_2 plus H_s obtained from decay curves following low-current density anodic pulses terminated at end of O sorption region (O_{ab} present)

increase i_r (see i_r values in Fig. 5a at comparable partial pressures), the lowering of H_2 partial pressure with increasing temperature (owing to increased partial pressure of water vapor) exerts a stronger effect than temperature.

The data in Fig. 5 were also taken under vigorous stirring conditions where increased stirring rates did not change i_r , therefore diffusion control of H_2 was minimized. The results shown in Fig. 5 indicate that the reaction mechanism for Eq. (4) must be quite different than for the case where O_{ab} is insignificant. The dependence on H_2 partial pressure indicates that the reaction is controlled by the chemical reaction of H_2 with O_{ad} . The tendency of a positive temperature dependence also indicates such a reaction control. The increase in i_r as $q_{O,ex}$ decreases shows that the reaction rate increases as the amount of sorbed O decreases, and the change to the higher slope at low $q_{O,ex}$ values indicates that the reaction step is becoming so fast that the overall rate, i_r , approaches the comparable values shown in Fig. 4 where O_{ad} migration is the indicated rate-controlling step. Hence, in the region of the steeper slope (Fig. 5) there appears to be a mixed control of the reaction. This is also verified by the coming together of the curves in Fig. 5 at the lowest $q_{O,ex}$ values. This indicates that H_2 partial pressure and temperature effects become less important as in the data shown in Fig. 4.

It is felt that the presence of O_{ab} in the Pt bead markedly lowers the heat of adsorption of O_{ad} . This in turn evidently slows the rate of the chemical combination of O_{ad} and H_2 .

One of the most important results of this investigation is considered to be the application of the described technique for separating differently sorbed species associated with a surface and determining their effects on the rates of chemical reactions. This technique can undoubtedly be applied to other systems.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the help of Professor P.H. Emmett of Johns Hopkins University, especially his suggestion that the surface migration of adsorbed species to active centers may be applicable for the reaction of O_{ad} with H_2 .

REFERENCES

1. Schuldiner, S., and Roe, R.M., J. Electrochem. Soc. 110:332 (1963)
2. Schuldiner, S., and Roe, R.M., J. Electrochem. Soc. 110:1142 (1963)
3. Warner, T.B., and Schuldiner, S., J. Electrochem. Soc. 111:992 (1964)
4. Nernst, W., and Merriam, E.S., Z. Phys. Chem. 53:235 (1905)
Sackur, O., Z. Phys. Chem. 54:641 (1906)
Breiter, M.W., Electrochim. Acta 7:601 (1962)
5. Breiter, M.W., J. Electrochem. Soc. 109:425 (1962)
6. Schuldiner, S., and Warner, T.B., J. Phys. Chem. 68:1223 (1964)
7. Franklin, T.C., and Cooke, S.L., Jr., J. Electrochem. Soc. 107:556 (1960)
8. Presbrey, C.H., Jr., and Schuldiner, S., J. Electrochem. Soc. 108:985 (1961)
9. Schuldiner, S., J. Electrochem. Soc. 106:891 (1959)
10. Schuldiner, S., Castellan, G.W., and Hoare, J.P., J. Chem. Phys. 28:16 (1958)