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# A Study of Adsorption and Oxidation of Carbon Monoxide on Platinum Using Constant-Current Pulses

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*Chemistry Division*

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# A Study of Adsorption and Oxidation of Carbon Monoxide on Platinum Using Constant-Current Pulses

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Using single anodic constant-current pulses, the steady-state concentration of both the carbon monoxide already adsorbed on the surface of a bright platinum electrode immersed in 1M $H_2SO_4$ and the additional amount of CO adsorbed during the application of the pulse has been determined. At potentials of 0.3 to 0.4 v relative to the normal hydrogen electrode, a surface coverage of one CO molecule per surface Pt atom was observed at very low CO partial pressures; for CO partial pressures up to 1 atm, the coverage increased to about 1.06 CO molecules per Pt atom, indicating that additional CO physically adsorbs on the base chemisorbed layer. At 1.0 to 1.3 v the rate of adsorption of CO was slower than the rate of diffusion (at 25°C), and indirect evidence suggests that CO is not adsorbed at potentials above 1.3 v.

The mechanism of oxidation of CO appears to be an electrochemical oxidation of water to form chemisorbed oxygen atoms, which then rapidly react with chemisorbed CO to form $CO_2$.

## INTRODUCTION

The amount of carbon monoxide that is adsorbed on platinum has been studied in the past under varying conditions. Most evidence is indirect, and results seem to be strongly dependent on the substrate. In the gas phase, some investigators have concluded that one atom of CO is adsorbed for each two Pt atoms (1), while others have found a 1:1 correspondence (2). Gilman (3) has studied the adsorption and oxidation of CO on a Pt wire in aqueous solutions using a potentiostatic method. He concluded that there was evidence of mixed linear and bridged adsorption.

The purpose of the present work was (a) to determine the extent of saturation surface coverage of a bright Pt electrode as a function of the partial pressure of CO in aqueous acidic solution, (b) to study the mechanism of oxidation of such adsorbed CO, and (c) to determine if the rate of transfer of CO from solution, during anodic charging, to an electrode partially covered with CO was diffusion or adsorption controlled.

## EXPERIMENTAL PROCEDURE

The cell, electrodes, helium and hydrogen purification systems, and general method used in the present work have been described elsewhere (4,5). The cell contained a Pt bead (99.99% pure) working electrode, a 90% Pt-10% Rh gauze electrode, and a Leeds and Northrup miniature glass reference electrode (4); also used were a palladium tube electrode (5,6) and a 5-cm-long platinum wire electrode (99.99%, 0.064 cm diam), not previously described, that, like the others, was mounted in Teflon and inserted into the cell through a glass nipple. Platinum bead electrodes with true areas of 0.177 and 0.289 $cm^2$ were used. True areas were defined using the method previously reported (5,7), which is based on a determination of the number of oxygen atoms deposited on the surface as a monolayer during anodic oxidation of water.

The electrolyte was 1M sulfuric acid (made with triply distilled water) maintained at $25 \pm 1$°C. While being stirred with either helium or hydrogen, the electrolyte was pre-electrolyzed periodically by making the Pt bead and gauze electrodes anodic (about 100 ma) relative to the Pt wire. At the end of the pre-electrolysis period (24 to 48 hours) the Pt wire electrode was removed from the cell (without disconnecting the current), dipped into concentrated nitric acid, then heated white hot in a hydrogen flame and replaced in the cell. The solution was then stirred with hydrogen until the potential between all pairs of platinum electrodes was equal to zero. At the same time, the glass electrode was calibrated against a $Pt/H_2$ normal hydrogen electrode (NHE),

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giving a potential of $-0.660 \pm 0.002$ v. The hydrogen flow was then replaced with helium.

After purification, the solution was stirred continuously with either helium or an appropriate gas mixture containing CO; a very slow stirring rate was maintained during application of charging pulses, except in the experiments on rate of diffusion of CO. Prior to each polarization pulse, the rest potentials (versus the glass reference electrode) of all the electrodes were determined with a Keithley 603 Electrometer. After the electrodes had again attained a rest potential, they were allowed to remain exposed to the CO-containing solution long enough to assure maximum adsorption of CO at each given CO partial pressure.

The Pt bead was anodized with single constant-current pulses (5) using an Electro-Pulse Model 3450D pulse generator; the counter electrode was, at first, the Pt-Rh gauze electrode. It was found, however, that under some conditions significant amounts of the hydrogen produced this gauze electrode would migrate to the Pt bead. To avoid this, the Pd tube electrode was substituted as the counter electrode. In this case, hydrogen produced on the surface of the Pd tube would migrate into the metal and be oxidized by oxygen in the air-space inside the tube (6).

Using the Pt wire as a reference electrode, the anodic charging curve of the Pt bead was photographed from the display on a carefully calibrated Tektronix 535 oscilloscope, which was recalibrated (for voltage and time) before each series of measurements. To evaluate possible transport effects, pulse current densities were varied from 56.1 to 2540 ma/cm$^2$. (All current densities reported here are on the basis of true electrode areas.)

To investigate the relative importance of the rate of diffusion of CO versus the rate of adsorption, charging curves were obtained in unstirred solution and in solutions stirred vigorously by bubbling in gas at rates well over 1000 ml/min; this rate of stirring was sufficient to cause the working electrode to vibrate rapidly. Tank carbon monoxide (C.P. grade) was introduced into the cell through a separate inlet after passing through a flowmeter, a dry-ice ethylene glycol monoethyl ether trap, and a water saturator. The gases used were (a) pure CO, (b) 9.89% CO in $N_2$(henceforth referred to as 0.1 atm partial pressure CO), (c) 0.0037% CO in He (referred to as 0.0037 atm partial pressure CO), (d) purified He, and (e) pure $H_2$. The first two gases were analyzed by means of a mass spectrometer and showed, respectively, $10 \pm 10$ ppm $H_2$ and less than 10 ppm $H_2$. The 0.0037 atm CO was prepared by mixing 0.1 atm CO with He. Total cell pressure was slightly above atmospheric.

Cleanliness of the Pt bead was checked from time to time, under CO-free conditions, by an anodic charging test (7), which is discussed in the Appendix. To prepare electrodes covered with adsorbed CO in solutions for which the CO partial pressure was zero, CO was admitted for varying periods of time (from 1 min to many hours), after which the cell was flushed with pure helium for 0.5 to 170 hours.

## RESULTS

### Anodic Charging Curves

Typical anodic charging curves for the Pt bead are shown in Fig. 1. The form of the curve was remarkably consistent over wide ranges of CO partial pressure and current densities.

A typical charging curve is sketched in Fig. 2, where potential changes in the CO oxidation region have been exaggerated to show fine detail. When a constant-current pulse is applied, the anode potential rises abruptly as the double layer capacitance is charged. After an initial potential overshoot (right-hand side of figure), the potential increases slowly to a rather constant value, which is maintained until the CO oxidation region ends (middle of figure). These details are apparent in low-current-density pulses but tend to be obscured in rapid sweeps made with high-current-density pulses. After adsorbed CO has been oxidized, the potential rises linearly as the Pt surface becomes covered with a monolayer of adsorbed oxygen atoms; upon completion of this monolayer, a new plateau (left-hand side of figure), which indicates the generation of molecular oxygen, is reached.

Potentials observed on open circuit and in the various portions of the charging curve are summarized in Table 1. (The latter potentials were obtained from measurements made on oscillograms.) The solution IR drop has been subtracted from all polarization potentials. The errors indicated are estimated limits of errors. The rather large error limits shown for the potentials at the

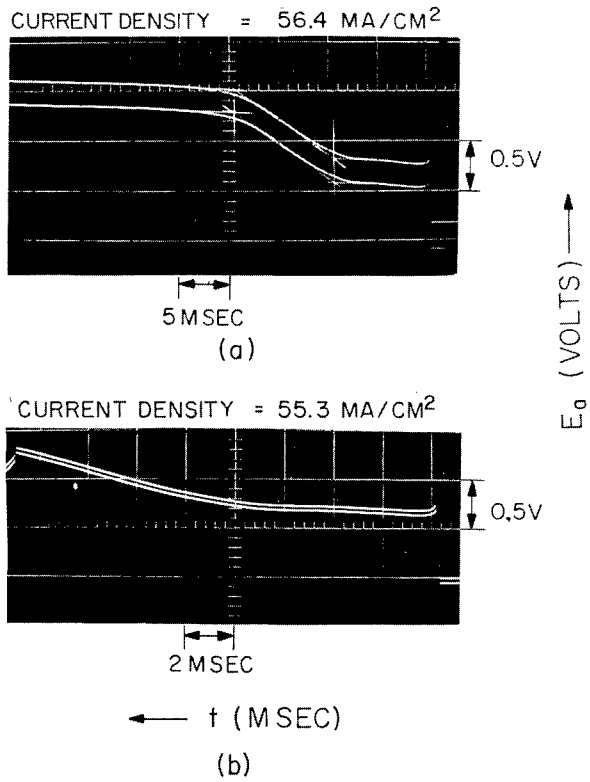


Fig. 1 — Representative anodic charging curves for the Pt bead showing oxidation of carbon monoxide. In oscillogram (a) the partial pressure $p_{CO} = 0.1$ atm; in (b) $p_{CO} = 0.0037$ atm. In each oscillogram the top trace was made in vigorously stirred solution, and the bottom trace was made in quiescent solution. Because of the faster sweep speed used in (b), the curve is expanded to show the lower CO plateau in more detail. $E_a$ is the anodic potential.

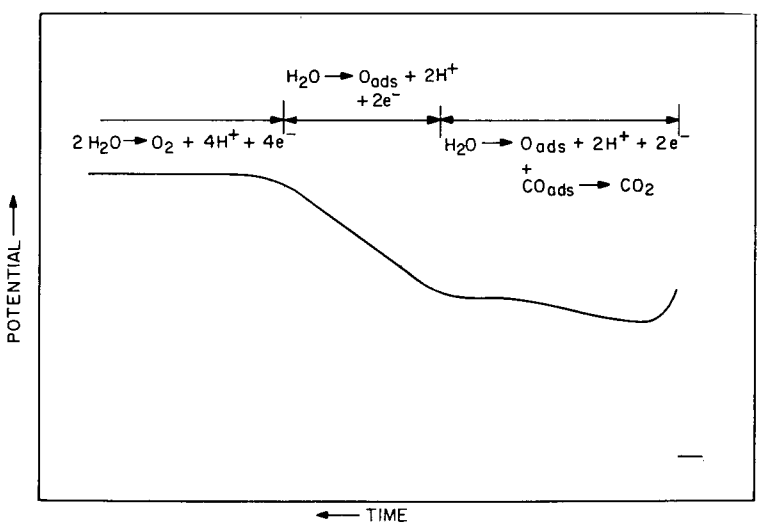


Fig. 2 — Sketch of a typical constant-current anodic charging curve obtained with a bright platinum electrode in 1M $H_2SO_4$ solution containing dissolved CO. The characteristics of the curve in the CO oxidation plateau region have been exaggerated to show fine detail.

TABLE 1
Platinum Bead Potentials Observed on Open Circuit and During Anodic Pulses

| Measured Potentials* (volts) | Partial Pressure of CO | | | |
|---|---|---|---|---|
| | 1.0 atm | 0.1 atm | 0.0037 atm | 0 atm |
| Open-circuit rest potential | 0.36 ± 0.02 | 0.36 ± 0.03 | 0.36† | 0.29 ± 0.04 |
| Potential at start of CO oxidation, $E_{CO}$ | 1.25 ± 0.13 | 1.18 ± 0.11 | 1.03† | 1.00 ± 0.11 |
| Difference between potential at start of CO oxidation and minimum potential during CO oxidation | 0.10 ± 0.01 | 0.08 ± 0.01 | 0.07† | 0.0 to 0.05 |
| Potential at start of O atom adsorption region | 1.25 ± 0.13 | 1.25 ± 0.14 | 1.03† | 1.09 ± 0.11 |
| Potential at start of $O_2$ evolution region | 1.81 ± 0.08 | 1.79 ± 0.08 | 1.69† | 1.67 ± 0.08 |

*With reference to the $Pt/H_2$ normal hydrogen electrode.
†Too little data to allow estimation of uncertainty.

start of the CO and O regions are partially due to the fact that these potentials were dependent on current density and increased slightly with increasing current density.

### Quantities of Charge Consumed in the CO Oxidation Region and the Oxygen Adsorption Region

The amount of charge transferred in the CO oxidation region and in the oxygen adsorption ($O_{ads}$) region was calculated by taking the product of current density and charging time (the time required to complete the particular oxidation process, as measured on the charging curve oscillograms). The amount $q_{CO}$ of carbon monoxide oxidized in the lower plateau region was calculated by taking the total number of coulombs per cm² transferred and subtracting the number of coulombs per cm² used to charge the double layer. In this case, although the potential was approximately constant over the entire CO region, the double layer capacitance changed as the layer of adsorbed CO was removed. The charge $q_{dl}$ consumed in charging the double layer was thus given by the relation

$$q_{dl} = E\Delta C \ (\mu\text{coul/cm}^2) \qquad (1)$$

where E is the potential in volts and ΔC is the change in capacitance in microfarads per cm² Based on relatively few measurements, the double layer capacitance of a Pt bead covered with CO is about 8 μf/cm². The capacitance at the end of the CO region should be that of a clean Pt electrode, *i.e.*, 40 μf/cm² (5). (This assumes that the $CO_2$ formed during the oxidation of CO either is not chemisorbed or, if sorbed, leaves the surface rapidly.) Hence, ΔC = 32 μf/cm².

The amount of charge $q_O$ used in oxidation processes in the O atom formation region was calculated similarly, with the charge going to the double layer being subtracted from the total charge transferred. In this case, the double layer capacitance C was taken to be 40 μf/cm² over the potential range traversed, and thus

$$q_{dl} = C\Delta E \ (\mu\text{coul/cm}^2). \qquad (2)$$

Values of $q_{CO}$ and $q_O$ obtained with different CO partial pressures $p_{CO}$ are plotted in Fig. 3 versus charging time t; the shortest charging times correspond to the highest current densities. Each point plotted in curves (a), (b), and (d) represents the average of four to sixteen determinations and is uncertain by about 20 μcoul/cm² (estimated standard deviation) for the plots of $q_{CO}$ and by 30 μcoul/cm² for the plot of $q_O$. Each point in curve (c) represents an individual determination. The arithmetic mean of the first four points of curves (a), (b), and (d, the solid black circles only) and of all the points of curve (c) are represented by horizontal lines; the numbers appearing above the lines are these mean values in microcoulombs per cm².

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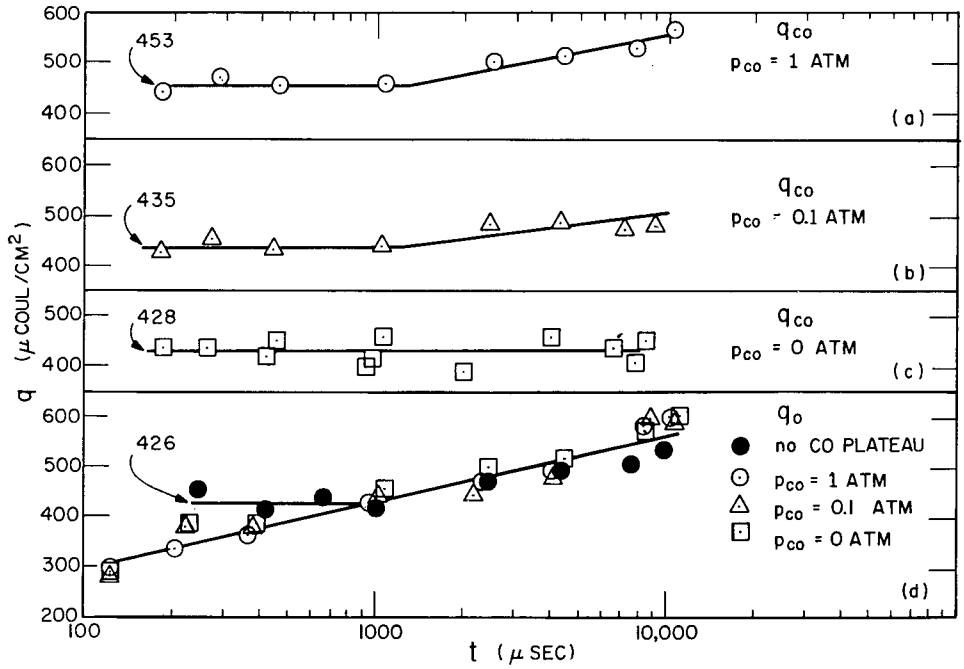


Fig. 3 — The amount of charge $q_o$ or $q_{co}$ transferred in each region of the anodic charging curves is plotted against the time required to complete the process in that region

## MECHANISM OF CARBON MONOXIDE OXIDATION

During the oxidation of CO, the amount oxidized was primarily that amount already chemisorbed on the anode; for the lower current density pulses, a slight additional amount of CO migrated to the electrode and was also oxidized. The fact that the electrode potential changed relatively little as CO coverage was reduced to zero suggested that direct electrochemical oxidation of CO was not taking place, for if it were, the potential would be expected to rise more sharply as the CO coverage decreased. The results suggest that the following processes are taking place at the platinum surface:

$$\text{I.}\quad Pt + H_2O \rightarrow Pt\text{-}O + 2H^+ + 2e^-$$

$$\text{II.}\quad Pt\text{-}O + Pt\text{-}CO \rightarrow Pt_2\text{-}CO_2$$

$$\text{III.}\quad Pt_2\text{-}CO_2 \rightarrow 2Pt + CO_2 \qquad (3)$$

$$\text{IV.}\quad CO_b \rightleftarrows CO_{dl}$$

$$\text{V.}\quad Pt + CO_{dl} \rightarrow Pt\text{-}CO$$

where Pt- signifies a species adsorbed on Pt, the subscript b is for the species in the bulk solution, and the subscript dl is for the species in the double layer. It should be remembered that essentially all of the Pt sites are normally covered with CO before application of an anodic pulse.

Experimental results indicate that the rate of step I is evidently equal to or slower than step II; otherwise, the oxygen concentration would increase with time, especially for the faster high-current sweeps, and the potential would steadily rise. (Previous work (5) has demonstrated that the potential of Pt in this region will be affected by the amount of adsorbed O on the surface.) The flatness of the CO oxidation region at all sweep speeds indicates that the number of adsorbed oxygen atoms remains effectively constant until all of the CO is removed. In addition, if step I were faster than II, an excess of adsorbed O could be formed at high current densities, which would result in more coulombs being consumed than at low-current-density pulses. This is directly contrary to the experimental results obtained.

Carbon monoxide oxidation took place at about 1.0 to 1.2 v, depending on CO partial pressure. This potential is near the low end of the oxygen

atom adsorption region (0.88 to 1.76 v) and supports the view that a small concentration of atomic oxygen is generated, which reacts with CO present on the electrode surface as fast as water is oxidized (step I). The fine structure of the charging curve in the CO region also supports this mechanism. For a dynamic system involving a sequence of several interdependent reactions, it is quite reasonable (8) that at the start of the reaction the concentration of a species may actually overshoot its ultimate steady-state concentration. After the double layer is charged by the pulse, the anode potential, which is believed to be a function of the atomic oxygen concentration on the surface of the electrode, overshoots and falls rapidly to some lower value. This shows an instantaneous excess of oxygen atoms on the surface. The oxygen atom concentration then falls to a lower steady-state value as the various reactant and product concentrations adjust themselves. Subsequently, when the degree of surface coverage $\theta$ of CO on the electrode is reduced to about two-thirds, the anode potential rises a little. This may represent a slight increase in the concentration of atomic oxygen which is required to maintain the oxidation reaction at the required rate as the CO coverage falls toward zero.

Another interpretation of the initial overshoot is that, because of the high electrode surface coverage with CO, a small amount of adsorbed CO is initially electrochemically oxidized. This will make bare a sufficient number of Pt sites so that the oxidation of water to adsorbed oxygen atoms then occurs, with subsequent chemical reaction with adsorbed CO. This latter reaction would then be favored because it goes at a somewhat lower potential.

## SURFACE COVERAGE OF PLATINUM WITH CARBON MONOXIDE

Figure 3 shows that, for a charging time longer than about 1000 $\mu$sec, as t increased (*i.e.*, as current density decreased) $q_{CO}$ increased. At times shorter than about 1000 $\mu$sec, $q_{CO}$ remained constant. The value of $q_{CO}$ obtained at the shortest charging times represents the charge required to oxidize the CO that was adsorbed on the electrode before the anodic pulse was applied. The increased $q_{CO}$ observed at longer charging times is due to oxidation of not only the initially adsorbed CO but also of the additional CO reaching the surface from the surrounding solution.

The numerical values given in Fig. 3 for the charge required to oxidize adsorbed CO are given in microcoulombs per cm². Because of the method used to define surface area, however, the quantities actually compared in determining the surface coverage of Pt with CO are the coulombs required to cover the surface with oxygen atoms (420 $\mu$coul/cm², based on the method used in Ref. 5) versus the coulombs required to oxidize CO adsorbed on the same surface. Since the same apparatus was used to measure both quantities, any instrumental errors will tend to cancel out, and the ratio of the two values should be much more accurate than either one individually.

The solid circles plotted in Fig. 3(d) represent values of $q_O$ obtained from charging curves of clean platinum (*i.e.*, with no CO adsorbed on the surface) in pure sulfuric acid solution. The amount of charge transferred remains constant for charging times up to 1000 $\mu$sec and represents the charge required to cover the surface of the Pt bead with oxygen atoms. At longer charging times, $q_O$ increases as some process removes oxygen atoms from the surface during the time of the pulse. This process could be the combination of oxygen atoms to form oxygen molecules, which could then diffuse into solution, or it could be the dissolution of adsorbed atoms into the bulk of the platinum. Since analysis of charging curves in quiescent solution and in rapidly stirred solution show no significant difference in $q_O$, the second process is probably dominant.

The area of the Pt bead was originally defined on the assumption that for each 420 $\mu$coul transferred (after correction for dl charging) in the oxygen-atom-adsorption region, 1 cm² of Pt area was covered. The average of a number of later measurements, shown in Fig. 3(d), is 426 $\mu$coul/cm²; this shows the reproducibility of such measurements.

Curves (a), (b), and (c) in Fig. 3 show that the amount of CO initially adsorbed on the surface of the anode increases somewhat with increasing CO partial pressure, and additional oxidizable material reaches the electrode at charging times longer than about 1000 $\mu$sec. In Fig. 3(c), for the case $p_{CO}$ = O, the charge required to oxidize

CO adsorbed at open-circuit rest potentials of 0.3 to 0.4 v was essentially the same as that required to deposit a monolayer of O atoms on the Pt bead when clean (428 $\mu$coul/cm$^2$ as compared to 426 $\mu$coul/cm$^2$); in this case, CO coverage is evidently unity (one CO molecule per surface Pt atom). The charge $q_{CO}$ is independent of charging time because there is virtually no additional CO in the solution to be adsorbed on the electrode during the charging pulse.

For CO partial pressures of 0.1 and 1.0 atm (Figs. 3(a) and (b)), surface coverage increased to about 1.02 and 1.06 CO molecules per Pt atom, respectively, indicating that additional CO physically adsorbs on the base chemisorbed layer. The relationship between the physically adsorbed CO and CO partial pressure is, within experimental error, in accordance with Henry's Law. At these partial pressures, $q_{CO}$ is larger at longer charging times because significant transport of CO from solution occurs.

The total amount of CO oxidized during a charging time of 10,000 $\mu$sec, when $p_{CO} = 1$ atm, is 550 $\mu$coul/cm$^2$; the excess over the initial surface coverage which must have migrated to the surface during the charging pulse is 97 $\mu$coul/cm$^2$. The corresponding excess for $p_{CO} = 0.1$ atm and 0.0037 atm is 68 and 12 $\mu$coul/cm$^2$, respectively.

To determine whether diffusion or adsorption of CO in solution was the slow process limiting the rate of increase of $q_{CO}$ as the charging time increased, charging curves were obtained for both quiescent and vigorously stirred solution. Since the rate of diffusion could be independent of rate of stirring if the diffusion layer is sufficiently thin, 0.0037 atm CO was used in these experiments to confirm the results obtained with higher CO pressures. While the thickness of the diffusion layer is an uncertain quantity, particularly under the conditions of this experiment, it was most certainly thick enough to be affected by the stirring rate used. At 0.0037 atm CO, the volume of solution that contains enough CO to contribute the excess of $q_{CO}$ observed (12 $\mu$coul/cm$^2$) may be computed, and from this the thickness of a reasonable diffusion layer may be computed. The layer was calculated to be about 1.4 mm thick in this, the most dilute solution used.* This result is substantially larger than the value usually assumed (about 0.2 mm in a system with natural convection and a vertical electrode) (10).

To minimize experimental errors, charging curves were alternately obtained for stirred and unstirred solution. Under no conditions did the average values of $q_{CO}$ in stirred and unstirred solution show significant differences, nor were the average values consistently higher in stirred solution than those in unstirred solution. Figure 1 shows typical results. In each of these oscillograms the bottom curve was taken in quiescent solution and the top curve was taken in solution which was stirred with gas flow rates well in excess of 1000 ml/min. The fact that the rate of migration of CO to the electrode is independent of stirring rate, even in very dilute solutions, shows that some process is slower than the diffusion of CO (Step IV, Eq. 3). The most probable rate-controlling step is the adsorption of CO (Step V, Eq. 3) on the surface of the electrode.

The diffusion coefficient $D_{CO}$ for carbon monoxide would be expected to be close to that of $N_2$ ($2.25 \times 10^{-5}$ cm$^2$/sec at 25°C (11)). Using this value for $D_{CO}$ and assuming, as a first approximation, that the conditions of semi-infinite linear diffusion (3, 12) prevail, then the amount $q_{diff}$ of CO which can diffuse to the electrode in the time of a charging pulse may be calculated. Expressed in terms of coulombs, and for the case where $p_{CO} = 1.0$ atm, this quantity becomes

$$q_{diff} = 0.96 \times 10^{-3}\, t^{1/2} \quad (\text{coul-sec}^{1/2}/\text{cm}^2). \qquad (4)$$

Equation 4 can give only a rough approximation of $q_{diff}$, however, because one of the assumptions underlying its use is that the concentration of the oxidizable substance at the electrode is equal to zero as soon as electrolysis has started. In our case, this isn't true until the end of the CO region. Thus, surface coverage $\theta_{CO}$ will vary between 1 and 0 as the CO region is traversed, and because the amount of extra CO being adsorbed on the electrode is small compared to the amount initially present, $\theta_{CO}$ will vary almost linearly with $t/t_{CO}$, where t is the time elapsed after the start of CO oxidation and $t_{CO}$ is the total charging time for the CO oxidation plateau. On the average, then, during the time of the charging pulse

*This assumes that the concentration of CO in the saturated 1M $H_2SO_4$ solution under 1 atm partial pressure is $9 \times 10^{-7}$ mol/cm$^3$ (9), that the concentration of CO under 0.0037 atm can be calculated by Henry's Law, that the Pt bead is a sphere whose true area is twice its geometric area, that the concentration gradient in the diffusion layer is linear, and thus that the thickness of the diffusion layer is twice the thickness of the layer which holds sufficient CO to account for the excess $q_{CO}$ observed.

in the CO oxidation region $\theta_{CO}$ will be about 1/2, and to a first approximation the amount of CO which would diffuse to the electrode under these conditions might be about (1/2) $q_{diff}$, as calculated from Eq. (4), or 48 $\mu$coul/cm$^2$ for a charging time of $10^4$ $\mu$sec when $p_{CO} = 1$ atm. The actual $\Delta q_{CO}$ observed was 97 $\mu$coul/cm$^2$, and since this was shown to be adsorption-limited, the rate of diffusion must be even larger. Therefore, in order to fit Eq. (4) to the experimental results, one would have to assume that the diffusion coefficient of CO in 1 M $H_2SO_4$ is appreciably higher than the value used. The alternate, and more likely, possibility is that this adaptation of the semi-infinite linear diffusion equation to this system is not valid.

## THE OXYGEN-ATOM ADSORPTION REGION

The number of coulombs per cm$^2$ transferred in the oxygen-atom-adsorption region is given in Fig. 3(d). For a clean Pt surface in $H_2SO_4$ and for charging times less than 1000 $\mu$sec, $q_O$ is constant and represents the charge required to deposit a single monolayer of O atoms on the surface, giving a 1:1 correspondence between O and Pt surface atoms. The values of $q_O$ for solutions containing CO is independent of CO partial pressure, suggesting that the increase in $q_O$ at long charging times is not due to adsorption and oxidation of additional CO on the surface. This is confirmed by the fact that $q_O$ is independent of stirring rate, which strongly indicates that in the potential range 1.3 to 1.8 v, CO is not adsorbed on Pt. The increase in $q_O$ to over 426 $\mu$coul/cm$^2$ at times longer than 1000 $\mu$sec is attributed to absorption of some of the O atoms formed into the surface layers of Pt (13), freeing fresh surface for the oxidation of additional water.

For charging times less than 1000 $\mu$sec, $q_O$ decreases steadily to values indicating formation of less than one monolayer of oxygen atoms. It is suggested that this is due to blocking of part of the surface by $CO_2$, which is formed in the CO-oxidation region and which has not had time to diffuse away from the surface. The fact that the $q_O$ equivalent to a full monolayer is obtained at charging times of about 1000 $\mu$sec indicates that, by this time, removal of $CO_2$ must be essentially complete.

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# Appendix

## A Method for Determining the Cleanliness of a Platinum Anode

Recent work at this laboratory showed that the linearity of the voltage-vs-time relation in the atomic oxygen adsorption region could be used as a reliable index of electrode cleanliness. Using a previously reported experimental technique (5), data, such as shown in Fig. A1, were obtained for a platinum bead electrode in 1M $H_2SO_4$. Figure A1 (a) shows four typical oscilloscope traces that are the result of four successive single anodic constant-current (0.454 amp/cm$^2$) pulses. The bottom curve was obtained with the platinum electrode after it has been partially covered with a small amount of carbon monoxide. The preparation of an electrode with only a fraction of its surface covered with CO was done by adding a small amount of CO to the electrolyte, lowering the partial pressure of the CO to zero by bubbling pure helium through the cell, and then removing the adsorbed CO by several anodic pulses. The minute amount of CO remaining in solution would then partially cover the Pt bead before the first anodic trace was taken.

For the bottom curve in Fig. A1(a), the region (Pt-O) in which oxygen atoms are formed shows a break, which indicates the oxidation of CO to $CO_2$. After the removal of CO, the potential rises as the electrode surface is covered with a monolayer of oxygen atoms until the upper plateau, which shows the generation of molecular oxygen, is reached.

The curve immediately above the bottom was taken 80 seconds after the first trace. This curve shows no evidence of CO on the electrode since the time interval between these first two pulses was not long enough to allow adsorption of a significant amount of CO from solution. The amount of charge transferred in the oxygen atom formation region is equivalent to a monolayer of oxygen, within experimental error, and agrees well with numerous other determinations made on clean surfaces (5). The shape of this curve is quite characteristic of the formation of a monolayer of atomic oxygen on a clean Pt surface. A very linear relation between potential and time is observed in the region for the formation of a monolayer of oxygen atoms. The time to gaseous oxygen evolution is longer in the bottom curve because extra charge is required to oxidize adsorbed CO.

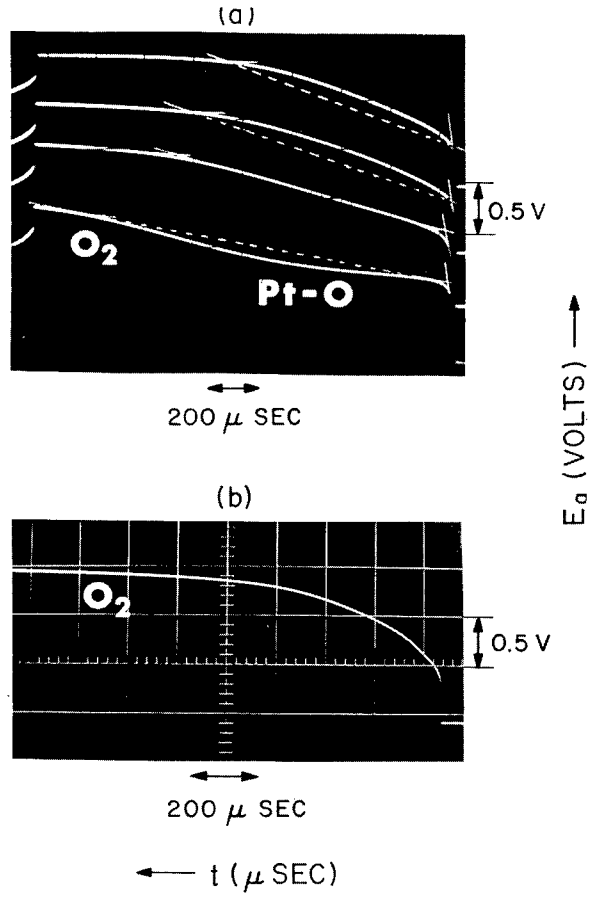


Fig. A1 – (a) Typical anodic charging curves (taken in succession); reading from bottom to top: first trace shows effect of partial coverage of Pt electrode with CO; second trace taken 80 sec later shows characteristic trace of a clean electrode; third trace taken 8 sec later shows effects of oxygen poisoning; and fourth trace taken 0.5 sec later shows additional oxygen poisoning effects. (b) Typical anodic charging curve poisoned with a nonoxidizable impurity (methane). $E_a$ is the anodic potential.

The third curve from the bottom in Fig. A1(a) was taken 8 seconds after the second pulse. Compared with the second pulse, fewer coulombs are required for the formation of the oxygen atom monolayer. This indicates that the time interval between the second and third pulses was too short to allow removal of all the adsorbed oxygen formed during the earlier pulse. The curve is also slightly convex in the oxygen atom region. This is believed to be due to oxygen

dissolved in the surface layers of the platinum, which could poison the discharge reaction.

These characteristics are more evident in the top curve of Fig. A1(a), which was taken about 0.5 second after the previous pulse. The oxygen adsorption region is even shorter and slightly more convex in this curve. This is because even less time elapsed between this and the previous pulse, and thus less oxygen was spontaneously lost from the surface. Also, there was a greater buildup of oxygen dissolved in the metal owing to repeated pulsing.

The four successive curves in Fig. A1(a) demonstrate that an impurity on the electrode which is oxidizable in the atomic oxygen formation region will cause a break in the linearity and an increase in the length of this region. If atomic oxygen is present on the electrode surface before the anodic sweep, it will be shown as a shortening of the atomic oxygen adsorption region, which gives a convex rather than straight-line relation in the same region. Substances, such as hydrogen, which are oxidized before the atomic oxygen formation potential is reached will be indicated as plateau regions at lower potentials (5).

Another, but less reliable, test of cleanliness of the electrode consists of a determination of the double-layer capacitance in the sharply rising potential region just before oxygen atoms are deposited. If a double-layer capacitance of about 40 $\mu$f/cm$^2$ (on the basis of true electrode area as defined by Schuldiner and Roe (5)) is found, this indicates that the electrode surface is clean. If the double-layer capacitance is significantly less than 40 $\mu$f/cm$^2$, then the presence of an impurity is indicated. If the double-layer capacitance is significantly greater than 40 $\mu$f/cm$^2$, the presence of a substance, such as hydrogen (5), which is oxidizable at potentials below the oxygen formation potential is indicated. This suggested test for surface cleanliness has an additional benefit. As shown by Schuldiner and Roe (5), the length of the atomic oxygen adsorption region can be used to define the true area of the clean platinum electrode.

The effect of a nonoxidizable impurity on the anodic charging curve is demonstrated in Fig. A1(b). For this curve, methane was added to the solution. Adsorption of this gas masked the surface so that no clear atomic oxygen adsorption region was found. No indication of oxidation of methane is apparent.

The importance of this test in kinetic investigations of the oxygen, or other, electrode process is apparent from a perusal of the literature, which shows such anodic charging curves. A careful reading of such curves shows that the presence of trace amounts of oxidizable impurities or of poisons in the atomic oxygen formation region is the rule rather than the exception. This test can undoubtedly be extended to other noble metals.