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Quarterly Status Report No. 7

RESEARCH RELATED TO MEASUREMENTS OF ATOMIC SPECIES IN THE EARTH'S UPPER ATMOSPHERE

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A. Introduction and Objective

Precise analysis by rocket- and satellite-borne mass spectrometers of the concentration of atomic oxygen in the earth's upper atmosphere is made difficult by the reactive character of the oxygen atoms themselves. These species can interact with solid surfaces by adsorption, by formation of oxides, and by catalytic production of molecular oxygen. Hence, the oxygen atom concentration as seen by a mass spectrometer may be substantially different from its real value in the environment because of atom removal on the surfaces of the instrument. The objective of this project is to elucidate the kinetics and mechanisms of interaction of oxygen atoms with solid surfaces of engineering interest under conditions similar to those encountered in the upper atmosphere. Such information will contribute to the quantitative interpretation of atomic-oxygen composition data reported by mass spectrometers in flight.

Our experimental approach employs a reaction vessel in which the total gas pressure and the entering flux of oxygen atoms are held constant. The rate of interaction of oxygen atoms with a metal surface is evaluated by observing the diminution in atom flux at the outlet of the vessel when a specimen of the material of interest is inserted into the reactor. The apparatus was described in Quarterly Status Report No. 4 (June 1, 1968), and the analytical basis of the experiment was discussed in Quarterly Status Report No. 5 (September 1, 1968). Results obtained with a gold-foil specimen were described and discussed in Quarterly Status Report No. 6 (December 1, 1968). The interaction of oxygen atoms with a silver surface is discussed here.

B. Experiments

1. Apparatus and Technique

The apparatus described in the preceding Quarterly Status Reports[1]

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[1] Quarterly Status Reports: No. 5, September 1, 1968; No. 6, December 1, 1968. Stanford Research Institute, Menlo Park, California, Contract NASr-49(30).

was used without modification. In the current experiments, the metal specimen is a ribbon of 99.999% pure silver foil, 23 cm long by 0.5 cm wide by 0.0038 cm thick. As in the earlier experiments, the specimen was suspended from its ends on electrical feed-throughs at the upper end of the reactor (Fig. 1). Before being installed in the reactor, the silver ribbon was lightly etched in an aqueous solution containing 10% ammonium persulfate and 10% potassium cyanide. Discolorations that remained after this treatment wer removed by lightly abrading the ribbon with a cotton swab coated with a slurry of 800 mesh aluminum oxide in water, then by thoroughly rinsing it in distilled water.

The quadrupole mass analyzer was calibrated before and after each experiment in the manner described in earlier reports.[1]

2. Measurements and Results

a. Atom Loss Coefficient for Silver

The efficiency by which oxygen atoms are removed from the gas phase (by any path, viz., sorption, occlusion, chemical reaction, or recombination) can be evaluated[1] by comparing the surviving atom concentration at the reactor exit aperture with and without the metal specimen in the reactor (n_1 and n_1^*, respectively). In terms of the fraction of atoms incident on the silver surface that are removed from the gas phase as atoms, this efficiency can be expressed as a loss coefficient L, where

$$L = [(n_1^*/n_1) - 1]/\sigma \quad .$$

The effective collision number of the specimen σ is the ratio of the specimen surface area A_s to the cross sectional area of the exit aperture A_e. This ratio is 24 for the silver specimen.

The loss coefficient calculated from the separation of the two curves drawn through the data points shown in Fig. 2 possesses a value L = 0.025.

b. Rate of Sorption of Oxygen Atoms on Silver

The mass of oxygen sorbed and occluded by the silver specimen at 300°K during exposure to gaseous oxygen atoms for a specific period of time, was evaluated after exposure by heating the ribbon to 725°K and measuring the mass of oxygen desorbed. By repeating a number of such measurements after exposure for varying time periods, the rate of sorption was determined. We have evidence that all the sorbed oxygen was not recovered during the two-minute heating period at this rather modest temperature. However, at temperatures in excess of 725°K the vapor pressure of silver attains values at which we could expect significant silver deposition on the reactor wall by evaporation.[2] To avoid this complication, we flashed at the stated temperature and measured the total amount of oxygen desorbed during a two-minute period. The results (Fig. 3) show that atomic oxygen is taken up by silver at 300°K at a constant rate well beyond monolayer coverage.

The total mass of oxygen sorbed or occluded by silver at 300°K appears to be linearly dependent on the pressure of gaseous oxygen atoms. The data shown in Fig. 4 represent the mass of oxygen sorbed during an exposure period of 10 minutes to atmospheres containing oxygen atoms at two different pressures.

c. Rate of Desorption of Sorbed Oxygen at 300°K

The rate of spontaneous desorption of oxygen from silver at 300°K was investigated by means of the flash-heating technique. The specimen was first exposed to atomic oxygen for precisely ten minutes to accumulate a specific occluded mass of oxygen (Fig. 3). The oxygen atom source (tungsten ribbon) was then cooled to a temperature at which thermal

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[2] R. W. Roberts and T. A. Vanderslice, Ultrahigh Vacuum and its Applications, Englewood Cliffs, N. J., Prentice-Hall, 1963, p. 85.

dissociation of oxygen was negligible, even though the total oxygen pressure in the system was not changed significantly. After a period of time the silver ribbon was flash heated and the quantity of oxygen desorbed was determined. This procedure was repeated for a number of different dwell periods up to 90 minutes in duration. The results are shown in Fig. 5 as the difference between the amount of oxygen atoms sorbed during an exposure of ten minutes' duration to atomic oxygen (Fig. 3) and the amount recovered during the heating flash after the specified dwell period in molecular oxygen.

It is evident that most of the atomic oxygen occluded by the silver is bound with sufficient strength to be completely stable at 300°K (compare Figs. 3 and 5). A portion of the oxygen associated with the solid corresponding to the equivalent of about one monolayer, is not so strongly bound, however, and desorbes rather rapidly at 300°K.

d. The Behavior of Impurity Carbon Monoxide

As in earlier experiments, carbon monoxide continued to be the major residual impurity in the high vacuum system. The installation of a new tungsten ribbon atom source during the middle of our experimental measurements with the silver specimen gave us the opportunity to evaluate the effect of this gas at various pressures. We determined that CO sorbs on silver rather slowly, exhibiting a sticking coefficient of 0.003 in CO partial pressures to 10^{-6} torr. We found no evidence that CO interferes with the uptake of oxygen by silver in an atmosphere containing atomic oxygen. Such behavior seems quite reasonable in view of the reported[3] results of other investigations of oxygen uptake by silver after pretreatment with carbon monoxide.

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[3] A. W. Czanderna, J. Phys. Chem., 68, 2765 (1964).

C. Discussion

The results of our study are most conveniently analyzed in terms of the kinetics of elementary processes[4] occurring at the surface of the silver. The following list associates these processes with mathematical expressions relating the rate of population or depopulation of oxygen on the surface to n, the concentration of gaseous atoms, and θ, the fraction of sites occupied by adatoms.

Sorption	$O(g) + (s) \xrightarrow{k_1} O(s)$	$\frac{d[O(s)]}{dt} = k_1(1-\theta)n$	(1)
Occlusion-Reaction	$O(s) \xrightarrow{k_2} O(\ell) + (s)$	$\frac{-d[O(s)]}{dt} = k_2\,\theta$	(2)
Recombination: Langmuir-Hinshelwood	$O(s) + O(s) \xrightarrow{k_3} O_2(g) + 2(s)$	$\frac{-d[O(s)]}{dt} = k_3\,\theta^2$	(3)
Recombination: Eley-Rideal	$O(s) + O(g) \xrightarrow{k_4} O_2(g) + (s)$	$\frac{-d[O(s)]}{dt} = k_4\,\theta n$	(4)

Based on equilibrium data, the probability of atom desorption from silver is virtually nil, so we need not consider the reverse of reaction 1. Also, the observed stability of the occluded oxygen phase suggests that the reverse of reaction 2 is negligibly slow relative to the other rate processes; hence it is not considered in this scheme. In addition, under the conditions of our experiments, we do not observe sorption of oxygen from the molecular state. Consequently, this process (the reverse of reactions 3 and 4) is eliminated from our consideration.

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[4] H. Wise and B. J. Wood, Advances in Atomic and Molecular Physics, 3, New York, Academic Press, 1967, p. 296ff.

Using these elementary steps and assuming a mass balance in a dynamic steady state, we can equate the rates of sorption and occlusion to the combined rates of recombination:

$$k_1(1-\theta)n + k_2\,\theta = k_3\,\theta^2 + k_4\,\theta n \tag{5}$$

Under the steady-state conditions of our experiments, the quantity of oxygen lost by spontaneous desorption at 300°K (Fig. 5) indicates that a fully populated monolayer of weakly sorbed atoms is maintained on the surface during exposure to atomic oxygen. Hence $\theta = 1$ and Eq. 5 becomes simply

$$k_2 = k_3 + k_4 n \tag{6}$$

The rate of occlusion k_2 (Fig. 3) and the rate of recombination by way of the Langmuir-Hinshelwood path, k_3, (Fig. 5) were measured experimentally. Substituting our data into Eq. 6 gives $k_4 n = 8.3 \times 10^{12}$ atoms$\cdot$cm$^{-2}\cdot$sec^{-1}, and $k_4 = 2.2 \times 10^{3}$ cm$\cdot$sec^{-1}.

The Eley-Rideal recombination coefficient γ is defined as the fraction of atoms colliding with the surface which recombine. From kinetic theory, the incident collision rate of gaseous atoms on a surface is $z = nc/4$, where c is the average velocity of the atoms. Therefore, $\gamma = 4k_4/c$, which leads to a value of $\gamma = 0.15$. This is in agreement with the value reported by Myerson.[5]

It is apparent that the overall loss coefficient L represented by $(1/z)(k_2 + k_3 + k_4 n)$ amounts to 0.38, which differs from the value determined from the data in Fig. 2 ($L = 0.025$). It is to be remembered

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[5] A. L. Myerson, Surface recombination efficiencies in flows containing step function increases in atomic oxygen, Cornell Aeronautical Laboratory Technical Report AF-2033-A1, Buffalo, N. Y., March, 1968

that the value in Fig. 2 is based on the ratio of the number of oxygen atoms leaving the empty reactor to the number leaving the reactor containing the silver specimen. In this calculation we assume that the glass reactor acts as a perfect reflector, an assumption which does not appear valid. Calculations based on the Monte-Carlo method have shown that even in the case of a perfectly noncatalytic wall the fractional mass transmitted is less than unity for cylindrical reactors of finite length.[6] Currently we are pursuing a theoretical analysis of this problem.

The nature of the occluded state cannot be determined from our measurements. The rather prolonged constant rate of uptake of oxygen exhibited by our specimen (Fig. 3) suggests that the occlusion process is not hampered by the formation of a discrete phase in the form of a layer of some silver oxide. On the basis of available thermodynamic data,[7] both AgO and Ag_2O would be stable at 300°K in the partial pressure of oxygen atoms attained in our experiments. McBee and Yolken,[8] using an ellipsometric technique, noted that film growth on a silver surface exposed to an undetermined flux of oxygen atoms was nearly linear with time up to a thickness of over 1000 Å. This indicates that the formation of a surface oxide phase cannot be ruled out as the mechanism of occlusion in our experiments.

D. Practical Conclusions

The insight into the interaction of oxygen atoms with silver obtained from our laboratory experiments may be of considerable value in interpreting the oxygen atom concentration data reported by the silver-plated mass spectrometer of the Explorer XXXII aeronomy satellite. The principal

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[6] H. A. Cohen, J. Vac. Sci. Tech., 5, 200, (1969).

[7] C. E. Wicks and F. E. Block, U. S. Bureau of Mines Bulletin 605, (1963); JANAF Thermochemical Tables, Dow Chemical Co.

[8] M. J. McBee and H. T. Yolken, Silver Oxidation in Atomic Oxygen, National Bureau of Standards Report 9802, March 25, 1968.

mode by which atomic oxygen is lost on silver under our experimental conditions appears to be occlusion in the bulk. The rate of this process, however, is dependent on the pressure of gaseous atoms (Fig. 4); hence, a continuous correction based on the variation of the ambient oxygen atom pressure would have to be applied to assess the significance of this process on atom loss.

We must also be concerned with the question of whether the silver foil surface exhibits the same oxygen atom loss characteristics as an electroplated, preoxidized silver film, such as that used in Explorer XXXII. We plan to examine such a surface in a later experiment.

E. Future Plans

Our immediate plans are to investigate the oxygen-atom interaction characteristics of titanium, which has also been employed in the inlet systems of satellite mass spectrometers.

F. Publications

A manuscript describing work carried out under this program has been prepared and is appended to this report. In the absence of any instructions from our sponsor to the contrary, we intend to submit this paper for publication in an appropriate scientific journal.

G. Personnel

Personnel who have participated in this program during the past quarter include Henry Wise and Bernard J. Wood.

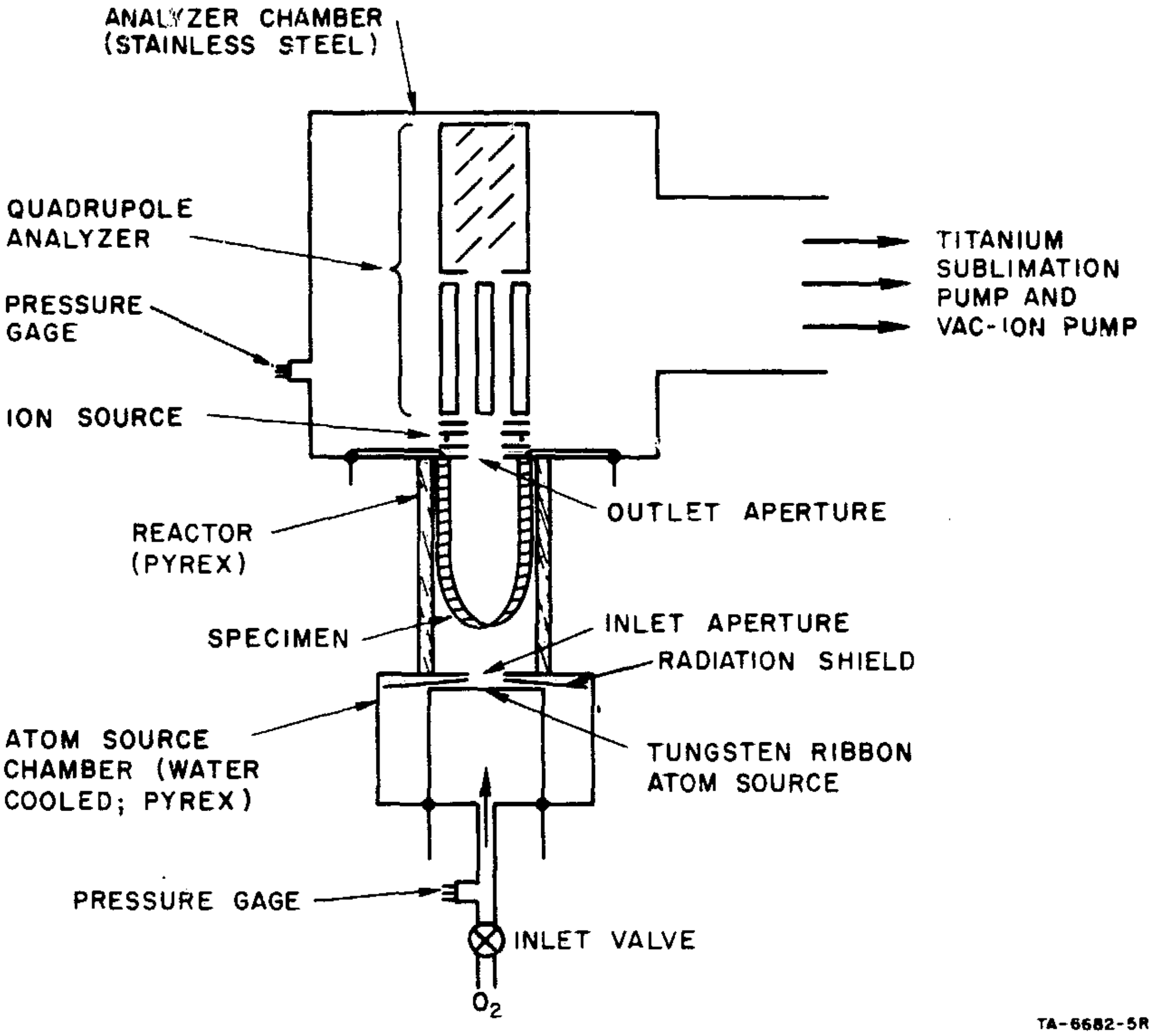

FIGURE 1 SCHEMATIC DIAGRAM OF APPARATUS

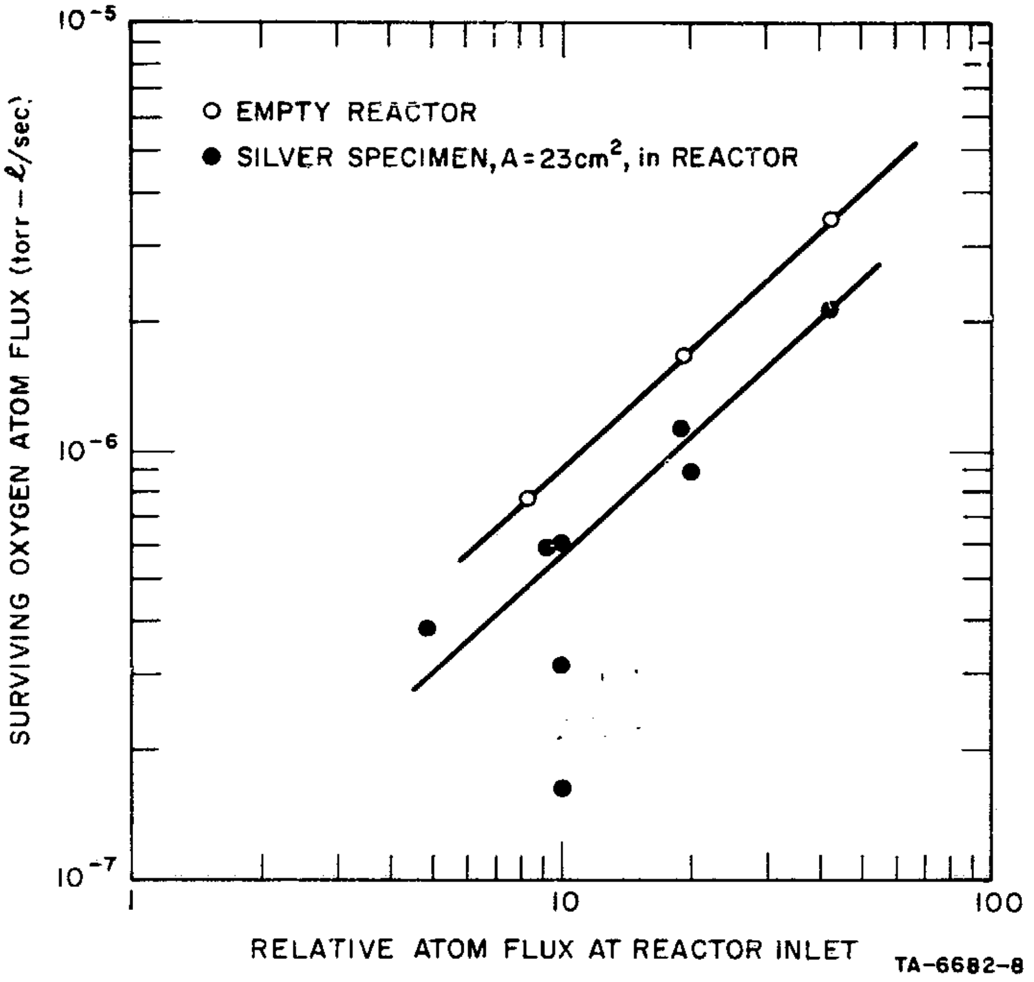

FIGURE 2 EFFECT OF PRESENCE OF SILVER SPECIMEN AT 300°K ON OXYGEN ATOM FLUX AT REACTOR EXIT APERTURE. Tungsten ribbon temperature: 2300°K.

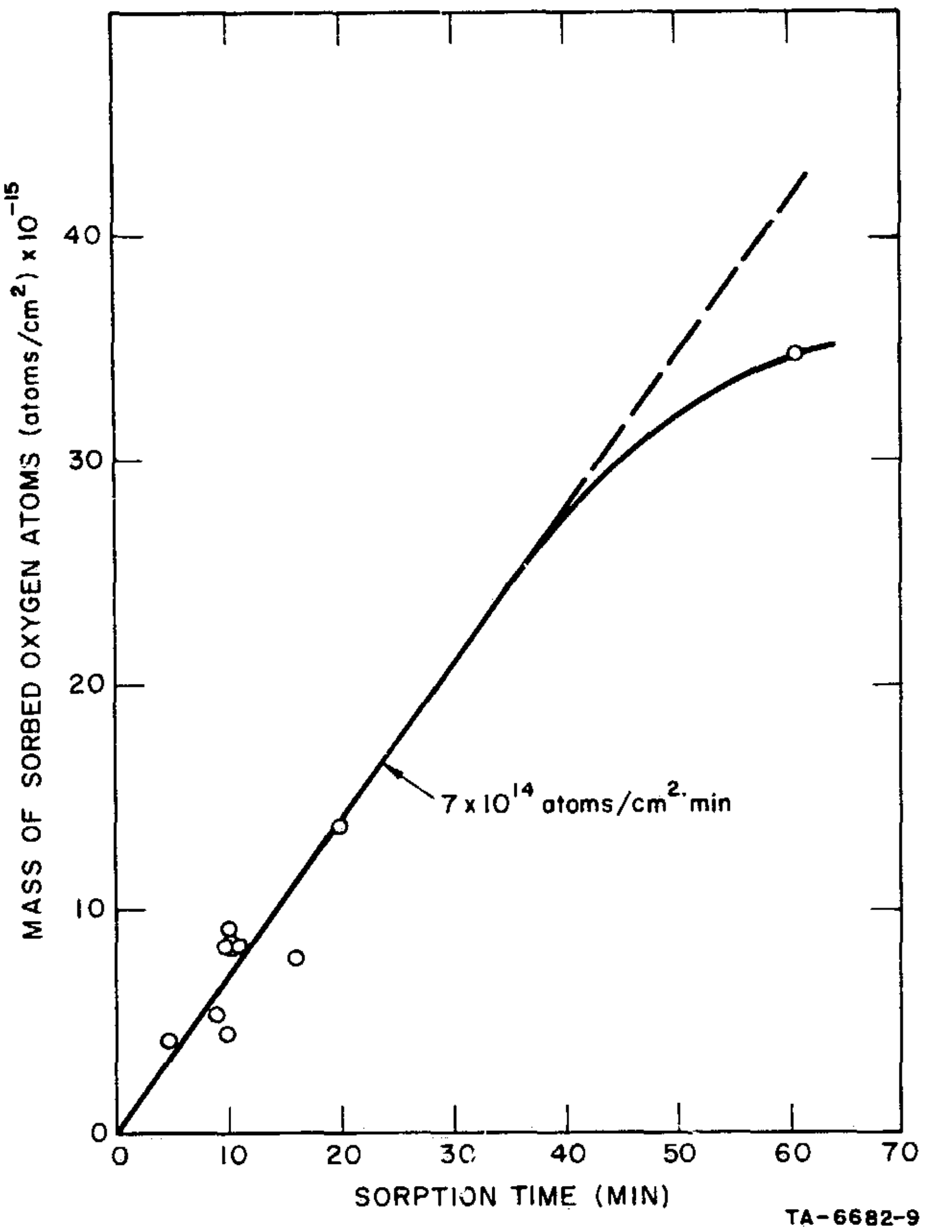

FIGURE 3 MASS OF OXYGEN ATOMS SORBED ON SILVER AS A FUNCTION OF EXPOSURE TIME. $P_0 = (1.2 \pm 0.5) \times 10^{-7}$ torr. $P_{O_2} = 10^{-6}$ torr. $T_{Ag} = 300°K$.

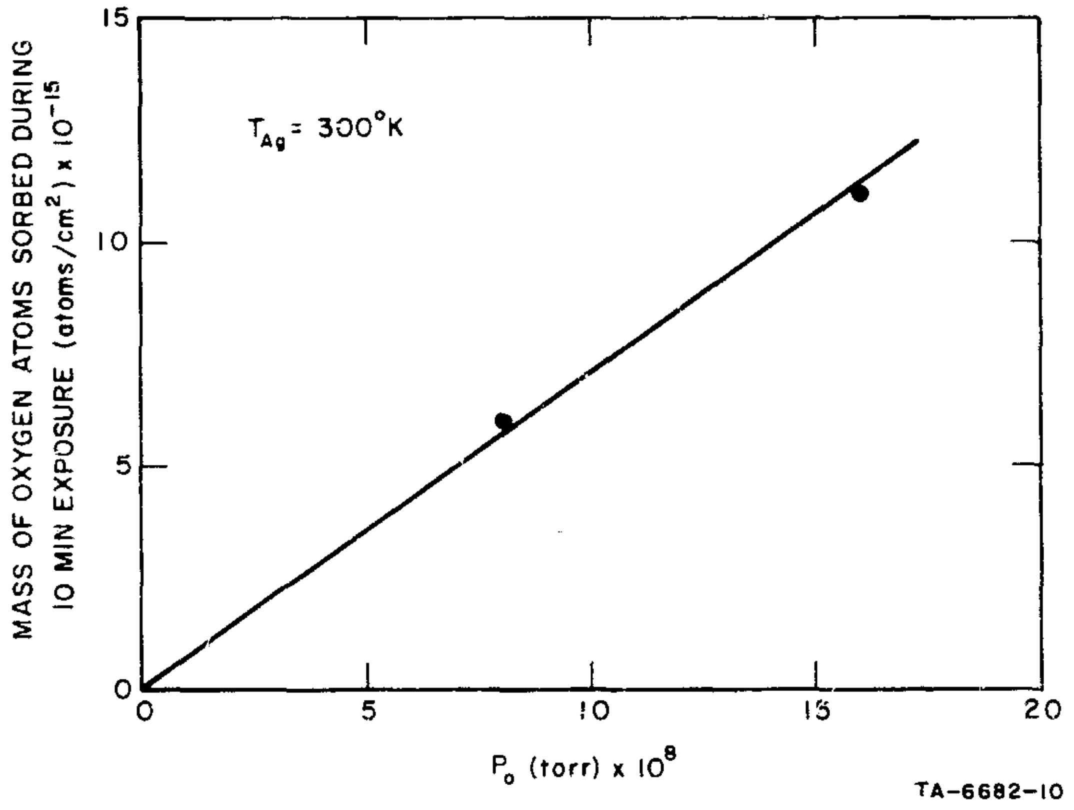

FIGURE 4 SORPTION/OCCLUSION OF OXYGEN ATOMS AS A FUNCTION OF PRESSURE.

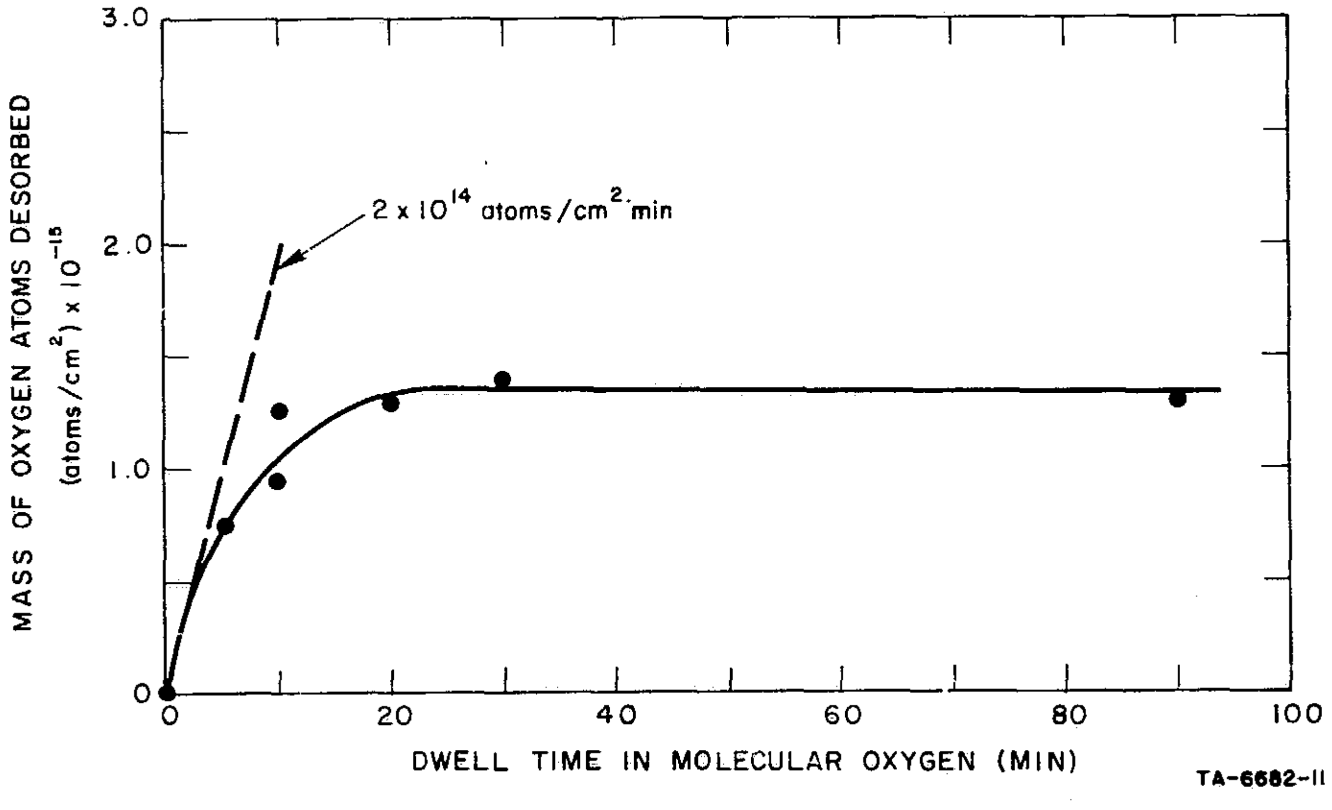

FIGURE 5 SPONTANEOUS DESORPTION OF OXYGEN FROM SILVER AT 300°K IN P_{O_2} = 2 x 10^{-6} TORR. At dwell time t = 0, silver had been exposed to gaseous oxygen atoms (P_O = 1.2 x 10^{-7} torr) for 10 minutes.

INTERACTION OF OXYGEN WITH PLATINUM[*]

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Abstract

The sorption of oxygen on a polycrystalline platinum ribbon has been studied with the aid of a quadrupole mass analyzer in an ultrahigh vacuum system in the pressure range from 5 to 10 x 10^{-8} torr. An evaluation of the reaction coefficient and the total mass of oxygen sorbed indicated that oxygen competes with carbon monoxide, present as a background contaminant (P $\simeq$ x 10^{-9} torr), for the sorption sites on the flash-cleaned platinum surface. Subsequent desorption of oxygen is not observed when the platinum is flash heated to temperatures up to 1100°K; carbon monoxide and carbon dioxide are the predominant species leaving the platinum surface. The relative amount of each component depends on the length of exposure of the flash-cleaned platinum ribbon to the background gas and to oxygen. The experimental results suggest a high reaction coefficient of oxygen on a clean platinum surface at room temperature (S $\simeq$ 0.2).

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[*] This research was supported by the National Aeronautics and Space Administration under Contract NASr-49(30).

Introduction

In view of the importance of the interaction between oxygen and metals in such areas as upper atmosphere composition studies, heterogeneous catalysis and catalyst surface-area determination, we have examined the adsorption and desorption characteristics of molecular oxygen on a clean platinum surface in a pressure region where rates of sorption can be conveniently measured ($\sim 10^{-7}$). We have also evaluated the role of an ubiquitous contaminant gas, carbon monoxide, on the kinetics and path of the sorption/desorption process.

Recent investigators have studied the surface chemistry of oxygen on platinum in the form of evaporated films,[1] foils,[2-4] single crystals,[5] and supported catalysts.[6-8] In all cases, a nonactivated process of chemisorption has been observed. The degree of surface coverage with oxygen has been a problem of major concern, with a limiting ratio of Pt/O = 2 generally assumed.

Experimental Details

The apparatus used for the experimental measurements (Fig. 1) was a Pyrex vessel consisting of two main sections (A and B) separated by shutter 1 and evacuated by separate ion-getter pumps. Chamber A (5 liters in volume) contained a quadrupole mass analyzer[*] which served the purpose of monitoring the pressure and composition of the gas mixture brought into contact with the platinum specimen. Chamber B (0.8 liter in volume), which contained the specimen, could be isolated from its pump by shutter 2. Both shutters were composed of two ground-glass discs, each pierced off center by a 3.5 cm diameter circular hole. One disc was attached to a central shaft and could be rotated relative to the other. The shutters were opened or closed by bringing the holes in or out of coincidence. Shutters 1 and 2 were ganged on a common shaft and so oriented relative to one another that when shutter 1 was open, shutter 2 was closed, and vice versa. The shutters were operated under vacuum by means of a "rotary-motion-feed-through."[†] The specimen was a ribbon of C.P. platinum foil (0.005 inch thick) spot-welded at its ends to glass-shielded tungsten wire supports. The ribbon, which had a geometric surface area of 2.4 cm^2, could be heated by passage of an electric current. Oxygen was admitted into chamber A from a high-pressure reservior (10 to 100 torr) through a servo-operated valve[§] and a fixed conductance F (Fig. 1). The outflow of reactant from chamber A was controlled by a valve (conductance f, Fig. 1) leading to the 50 liter sec^{-1} ion getter pump.

Pressure measurements were made with inverted Bayard-Alpert type ionization gauges operated with low temperature thoria-on-iridium

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[*] Manufactured by EAI, Palo Alto, Calif.

[†] Ultek Corp., Palo Alto, Calif.

[§] Granville-Phillips Automatic Pressure Controller.

filaments. The mass spectrometer was calibrated with oxygen against ion gauge 2 in the range of 5 x 10^{-9} to 1 x 10^{-6} torr. The readings were found to be linearly related at pressures greater than about 5 x 10^{-8} torr for emission currents of 0.1 and 1.0 mA.

The experimental ratios of the pressures indicated by gauges 1 and 2 (Fig. 1) corresponded to those calculated from mass flow considerations. These results demonstrated that the pumping characteristics of the two gauges were similar in the range employed.

The gas-handling system could be operated in two modes: (1) the constant-flow condition, by fixing the rate of flow of reactant into chamber A, and (2) the constant-pressure condition, by controlling the leak rate through the servo-operated valve with signals received either from the total pressure gauge (ion gauge 2, Fig. 1) or from the quadrupole mass spectrometer (Fig. 1). Both modes of operation were employed in our experimental measurements.

In a typical constant-pressure experiment, a steady state pressure of oxygen at 1 x 10^{-7} torr was established in chamber A, while at the same time, the platinum ribbon in chamber B was cleaned by flash heating at 1100°K for 30 sec. A time interval of 120 sec was allowed for cooling of the ribbon to room temperature in a background pressure of 5 x 10^{-9} torr. Subsequently, chambers A and B were connected by closing shutter 2 and opening shutter 1, while the pressures monitored by ion gauges 1 and 2 were continuously recorded. The rate of sorption of oxygen on the platinum specimen (and the walls of chamber B, see below) was

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* General Electric Co., Schenectady, N.Y.

reflected in the observed change in gas flow into the system through the inlet conductance F. The sorption rate, R, is given by

$$R = F(P_1 - P_1') \qquad (1)$$

where P_1' denotes the oxygen pressure in gauge 1 prior to exposure of the specimen, and P_1 that at time t. In addition, the total mass, M, of gas adsorbed at any time was evaluated by intergration of the area of the curve of P_1 versus time

$$M = \int_0^t F(P_1 - P_1')\,dt \qquad (2)$$

The sequence of operations for the sorption experiments under isobaric conditions is presented in Table 1.

A blank experiment was carried out to determine the extent of oxygen sorption by surfaces other than the platinum specimen, such as the walls of chamber B. After completion of step 7 (Table 1) of the sorption measurement, chamber B was isolated and evacuated to the background pressure (5×10^{-9} torr) without flash cleaning of the platinum specimen. Subsequently, chambers A and B were connected (steps 5 and 6, Table 1). The mass of gas sorbed under these conditions was attributed to wall pumping since the platinum ribbon was covered with oxygen from the preceding experiment.

In the constant-flow experiments, the sorption process was followed by monitoring the decrease in total pressure and partial pressure of O_2 as a function of time by means of ion gauge 2 and the mass analyzer set at amu 32. The downstream conductance f was evaluated in the conventional manner by calculating the mass flux from the steady state pressure readings at ion gauges 1 and 2. The wall pumping correction was made in a manner similar to that used in the isobaric experiments.

Desorption data were obtained both in the presence and absence of oxygen under constant-flow conditions. Desorption was accomplished by flashing the sample ribbon at the same temperature and at the same rate as in the initial cleaning procedure with shutter 1 open and with conductance F fixed (steps 6-10, Table I).

Results

The kinetic results obtained in a typical experiment for the sorption of oxygen on "clean" platinum are shown in Fig. 2. These measurements refer to the constant-pressure mode of operation at two platinum temperatures and various lengths of heating time during flash cleaning. The sorption kinetics are expressed in terms of a reaction coefficient, S, which represents that fraction of the incident molecules which adsorb (or react) on the surface.[4,9]

$$S = R/ZA \tag{3}$$

where Z is the collision frequency and A the geometric area of the platinum specimen.

Since Z may be expressed in terms of the product of the impingement rate ν (torr-liter sec^{-1}) and the oxygen pressure, one obtains by substitution from Eq. (1)

$$S = [F(P_1 - P_1')]/(A\nu P_2) \tag{4}$$

In the experiments just described, ion gauge 2, which reflects the total pressure in the system, controlled the mass flux into the system at any time during the constant-pressure sorption measurement. In other experiments, the signal of the mass analyzer set at amu 32 was employed to govern the influx of oxygen into the system as demanded by the sorption process for constant-pressure operation. All other conditions including the cleaning procedure were maintained. At a steady state pressure of oxygen of 1×10^{-7} torr, the platinum surface at 298°K sorbed 1.7×10^{-6} torr-liter of O_2 which compares favorably with a value of 2.3×10^{-6} torr-liter observed with the ion gauge. The difference is undoubtedly due to the different response of the two instruments to CO present as a background contaminant.

Of considerable interest are the results obtained from a series of desorption measurements. During these studies the total gas pressures (measured by ion gauge 2) and the partial pressures of several components (measured by the mass analyzer) were monitored as the platinum ribbon temperature was rapidly raised to 1110°K after completion of the sorption process at 298°K. No oxygen was desorbed from the surface when the ribbon heating was carried out in the presence of molecular oxygen ($P_{O_2} = 10^{-7}$ torr) at a steady state flow. As a matter of fact, the quadrupole mass analyzer showed that the partial pressure of oxygen diminished and the partial pressures of CO and CO_2 increased. In another experiment in which the ribbon was heated in a system evacuated to $<10^{-8}$ torr, similar results were obtained, i.e., no liberation of O_2 but desorption of CO and CO_2.

The relative distribution of CO and CO_2 appeared to depend on the time interval between flash cleaning of the platinum ribbon at a base pressure of 5×10^{-9} torr and exposure to a given gas pressure of O_2. It can be seen from the data presented in Table 2 that (1) the mass of O_2 sorbed decreases with dwell time of the platinum specimen in the background gas (at 5×10^{-9} torr), (2) the mass of CO_2 desorbed attains a maximum value, and (3) the mass of CO desorbed increases. The origin of the CO in the system is not known precisely, but the mass analyzer indicated that at the base pressure of 5×10^{-9} torr about 80% (by volume) of the residual gas is carbon monoxide.

Discussion

Since the oxygen sorbed on the platinum specimen is not recovered as O_2, we conclude that chemical reaction occurs on the surface between the oxygen and the platinum and other sorbed species. Based on the observed residual partial pressure of CO in the vacuum system and on the identification of the desorbed gas as CO_2, we conclude that a primary chemical process occurring on the surface is the catalytic oxidation of CO to CO_2.

The disparity in the mass balance between sorbed and recovered gas (Table 2) can be accounted for by proposing a second chemical reaction at the surface to form a platinum oxide[10] (such as PtO or PtO_2). Platinum oxides are known to be volatile[11] under the conditions of temperature and oxygen pressure employed in our experiments. Hence, it seems likely that, upon heating, the fraction of the surface-sorbed oxygen which does not react with sorbed CO volatilizes as PtO or PtO_2. These species would be present at concentrations below the limits of detection of our apparatus and could condense on adjacent cool surfaces.

The diminution in mass of oxygen sorbed with increasing dwell time of the cleaned specimen in the evacuated system suggests that CO sorption pre-empts sites that would otherwise be available for oxygen. For reaction to occur, both O_2 and CO need to be chemisorbed. The data suggest that CO_2 is not chemisorbed at room temperature.

On the basis of these observations a mechanism may be postulated to describe the interaction of oxygen with a platinum surface·

CO sorption	$CO(g)$	$\rightarrow$	$CO(s)$
Flash desorption preceding O_2 sorption	$CO(s)$	$\rightarrow$	$CO(g)$
O_2 sorption	$\begin{cases} O_2(g) \\ O(s) + CO(s) \end{cases}$	$\rightarrow$ $\rightarrow$	$2O(s)$ $CO_2(s)$
Flash desorption following O_2 sorption	$\begin{cases} O(s) + Pt \\ CO_2(s) \end{cases}$	$\rightarrow$ $\rightarrow$	$PtO(g)$ $CO_2(g)$

To obtain some measure of the energy of adsorption of CO on Pt, we carried out a series of experiments in which the maximum temperature attained by the platinum ribbon during flash cleaning was limited to 815°K rather than 1100°K. Under these conditions, no subsequent uptake of oxygen by the ribbon could be detected. Using the "rule of thumb" that desorption occurs at a significant rate[12] when the specimen temperature is greater than $20(Q_d)$, where Q_d is the heat of adsorption, one obtains a value of $41 < Q_d < 55$ kcal/mole.

The value for the reaction coefficient of oxygen on platinum at 298°K is of the same magnitude as that reported by Vanselow and Schmidt[3] on a platinum ribbon. However, S appears to be strongly affected by the length of time the platinum filament was heated to 1100°K during the flash desorption step (Fig. 2). Similarly, the total mass of gas sorbed is a function of the duration of flash cleaning of the platinum ribbon at a background pressure of 5×10^{-9} torr (Table 3). As a matter of fact, there appears to be a proportionality between the mass of oxygen sorbed, M, and the reaction coefficient, S, as evidenced by the constant value obtained for the ratio M/S (Table 3). On the basis of these results, we conclude that the duration of flash cleaning at 1100°K was insufficient to completely remove the gases sorbed on the surface of our platinum ribbon. Undoubtedly the strong binding of chemisorbed oxygen by platinum, for which process an energy of adsorption of 67 kcal/mole has been reported,[1] is reflected in this result. Also, the temperature gradients in the platinum ribbon during flash heating add to the problem of completely removing the sorbed layer.

Several investigators[3,5] have reported that the upper limit of sorbed oxygen coverage corresponds to a ratio Pt/O = 2. This degree of surface coverage would correspond to 6×10^{14} atoms/cm^2, assuming 1.2×10^{15} Pt atoms/cm^2 on the basis of a surface area of 8.1 Å^2/Pt atom, averaged over the various crystal orientations.[13] The highest surface density of adsorbed atoms attained in our experiments was 2×10^{14} atoms/cm^2. If the relationship between total mass sorbed and reaction coefficient were to be maintained up to a surface overage of 6×10^{14} oxygen atoms/cm^2, one would expect an initial value of $S = 0.2$. Such reaction coefficients are comparable to those obtained for hydrogen on platinum.[14] Our experimental results confirm the nonactivated chemisorption of oxygen on platinum as is found to be the case with hydrogen.

As for the competitive and pre-emptive adsorption of carbon monoxide, the data obtained emphasize the problems associated with oxygen sorption on platinum as a method for surface-area determinations. Obviously the product of reaction coefficient and partial pressure of gas need to be considered in an evaluation of the relative importance of the sorption kinetics of the individual gaseous components. In a conventional vacuum system operating at moderate background pressures of 10^{-6} to 10^{-5} torr, of which a large proportion may be made up of carbon monoxide with a reaction coefficient approaching unity, one can expect up to 10^{15} sites occupied each second. Thus for a supported catalyst with platinum surface area of 1 m^2 complete coverage might be expected within about 100 minutes of exposure to the background. It must be concluded therefore that prolonged exposure of a platinum catalyst to the background gas of a vacuum system operating at 10^{-6} torr may lead to high carbon monoxide coverage that will falsify the surface area determination on subsequent sorption of oxygen.

References

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2. O. V. Krylov and S. Z. Roginskii, Dokl. Akad. Nauk SSSR 88, 293 (1953).
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Table 1

EXPERIMENTAL PROCEDURE

Operation	Inlet Valve	P_2[a] (torr)	P_3[a] (torr)	Shutter 1	Shutter 2	Specimen Temp.(°K)
(1) Starting condition	Closed	$<5 \times 10^{-9}$	$<5 \times 10^{-9}$	Closed	Open	298
(2) Inlet valve control set to admit O_2 and stabilize P_2	Open	1×10^{-9}	$<5 \times 10^{-9}$	Closed	Open	298
(3) Specimen heated (cleaned)	Open	1×10^{-7}	Peaks	Closed	Open	1113
(4) Specimen cooled	Open	1×10^{-7}	$<5 \times 10^{-9}$	Closed	Open	298
(5) Sorption commenced. Rate of sorption and quantity sorbed measured by recording P_1	Open	1×10^{-7}	1×10^{-7}	Open	Closed	298
(6) Sorption completed	Open	1×10^{-7}	1×10^{-7}	Open	Closed	298
(7) System evacuated	Closed	1×10^{-8}	1×10^{-8}	Open	Closed	298
(8) Specimen heated (desorbed); total quantity of all gas desorbed evaluated from ΔP_2; identity of gas established with quadrupole analyzer	Closed	Peaks	Peaks	Open	Closed	1113
(9) Specimen cooled	Closed	1×10^{-8}	1×10^{-8}	Open	Closed	298
(10) Starting condition restored	Closed	$<5 \times 10^{-9}$	$<5 \times 10^{-9}$	Closed	Open	298

[a] Subscripts refer to ion gauges identified in Fig. 1.

Table 2

EFFECT OF BACKGROUND GAS ON OXYGEN SORPTION BY PLATINUM AT 298°K

(Base pressure = 5×10^{-9} torr, oxygen pressure = 1×10^{-7} torr)

Dwell Time after Flash Cleaning (sec)	Mass of O_2 Sorbed (torr-liter $\times 10^6$)	Mass Desorbed[a]/ (torr-liter)		
		amu 28	amu 32	amu 44
120	2.3	0.2	0	1.5
240	1.9	--	0	4.5
600	1.6	--	0	2.9
3,000	0.6	16	0	--
300,000	0	20	0	--

[a] Quadrupole mass analyzer calibrated using O_2 with ion gauge.

Table 3

EFFECT OF FLASH-CLEANING TIME ON OXYGEN SORPTION BY PLATINUM RIBBON AT 298°K[a]

Flash-Cleaning Time at 11000°K (sec)	Mass O_2 Sorbed at Saturation, M (atoms/cm^2 $\times 10^{-13}$)	Pt/O[b]	Reaction Coefficient S	M/S $\times 10^{-15}$
30	6.5	18	0.023	2.8
155	15.0	8	0.063	2.4
180	18.4	6	0.075	2.5

[a] The platinum ribbon was allowed to cool for 120 sec before exposure to oxygen at $P = 5 \times 10^{-8}$ torr.

[b] Based on 1.2×10^{15} surface atoms of Pt per square centimeter of area.

Figure Captions

Fig. 1 Schematic diagram of experimental apparatus

Fig. 2 Reaction coefficient of oxygen on platinum as a function of surface coverage and temperature

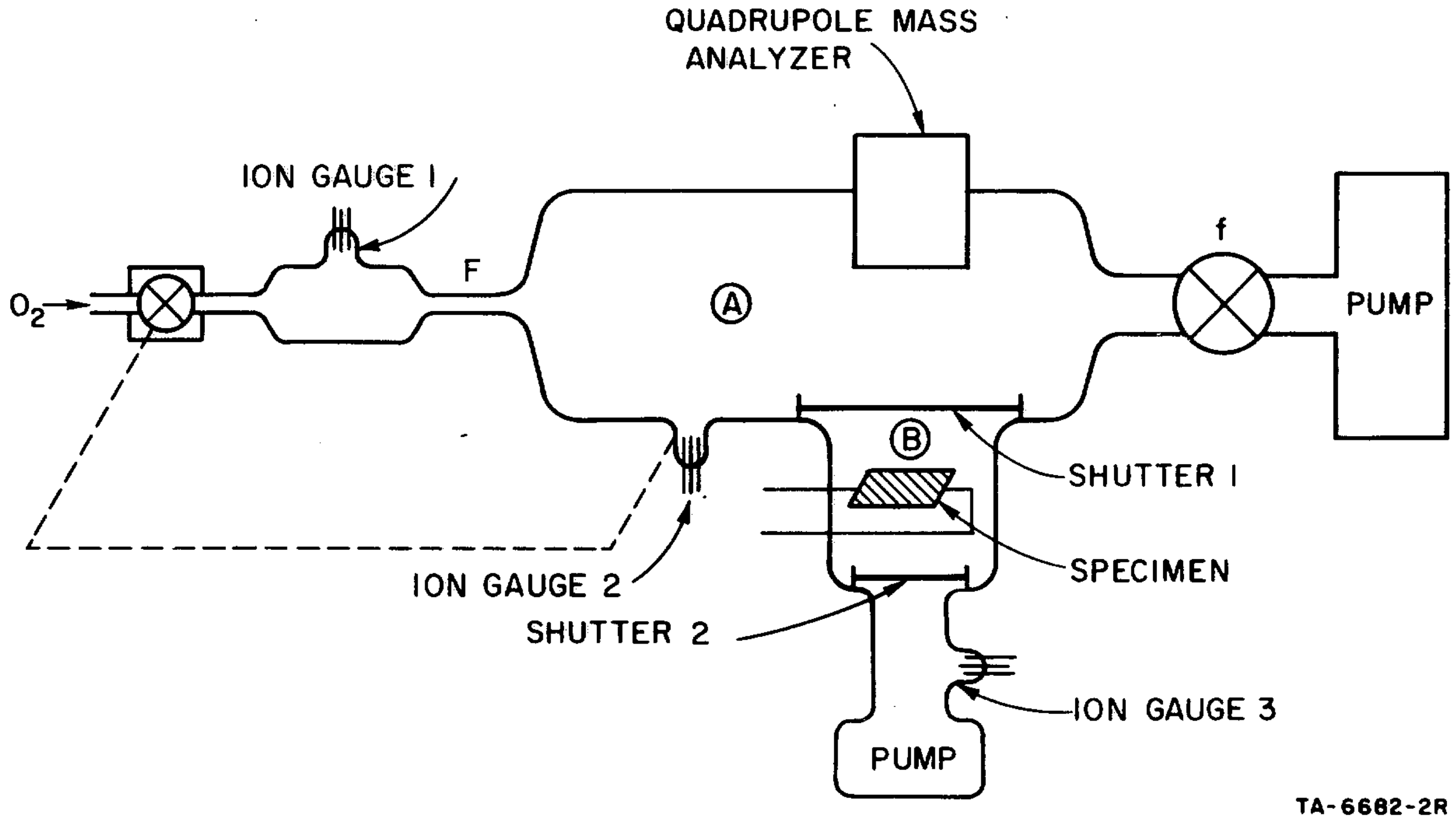
QUADRUPOLE MASS ANALYZER
ION GAUGE I
O_2
F
Ⓐ
f
PUMP
Ⓑ
SHUTTER I
SPECIMEN
ION GAUGE 2
SHUTTER 2
ION GAUGE 3
PUMP
TA-6682-2R

FIG. 1

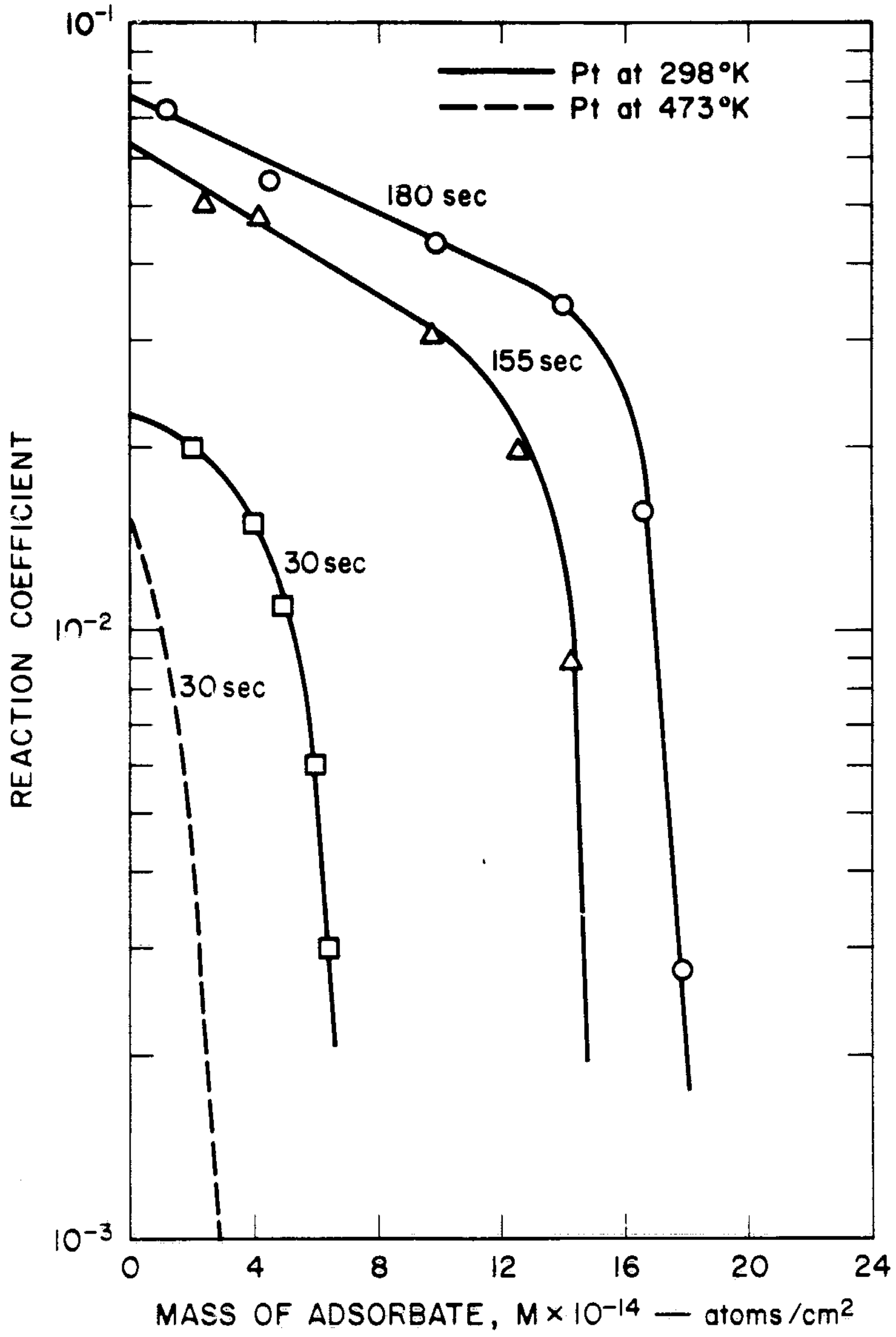

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FIG. 2