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

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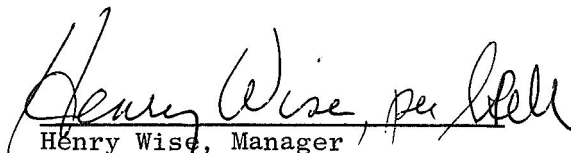
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A. Introduction and Objective

Quantitative analysis by rocket- and satellite-borne mass spectrometers of the atomic oxygen density in the earth's upper atmosphere is made difficult by the reactive character of the oxygen atoms. 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. Our preceding reports have described and discussed the kinetics of interaction of oxygen atoms with a number of metal surfaces which have been employed in the fabrication of flight mass spectrometers. These metals included gold, silver, titanium, aluminum, and stainless steel. Recently we have studied the interaction of hydrogen atoms with gold and oxygen-covered gold. In addition, we have carried out experiments with oxygen atoms in a reactor of modified geometry to provide a direct test of our analytical model.

B. Experimental Results and Discussion

1. The Interaction Kinetics of Hydrogen Atoms with Gold

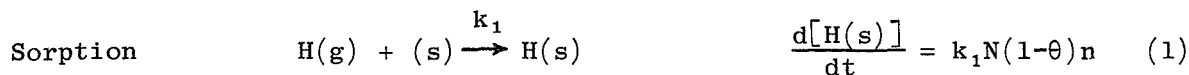
Based on our earlier work¹, the surviving flux of hydrogen atoms through the outlet of our reactor is reduced by approximately one-half when a 23-cm² gold ribbon is inserted into the reactor. Flash-filament measurements of the rate of adsorption of hydrogen atoms on gold under

similar conditions of temperature and pressure indicate that at steady state less than 10% of the metal surface is populated with adsorbed hydrogen atoms.¹ This low surface coverage seemed insufficient to account for the apparently high total loss of atoms on the gold surface; hence we performed additional experiments to investigate the dependence of the surface kinetics on atomic hydrogen pressure and coverage.

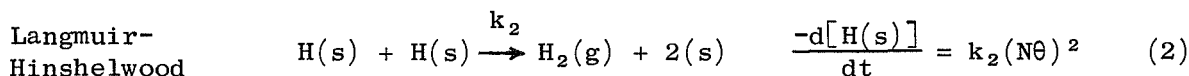
As before, we employed the flash-filament technique.² We varied the atom partial pressure by changing the total hydrogen flux through the reactor. This affects both atomic and molecular hydrogen pressures in the reactor, but the rate of adsorption of molecular hydrogen on gold is negligibly small at the temperature of our experiment (25°C). Figure 1 shows the surface coverage as a function of time for various H atom pressures. The results show the steady-state surface coverage increases with the pressure of atomic hydrogen. The initial rate of adsorption on clean gold, however, seems to be first order with respect to atom pressure within the precision of our pressure measurements. The calculated sticking coefficients are shown in Fig. 2. They are in agreement with the previously reported¹ values at low surface coverages.

We also measured the rate of desorption of hydrogen (as molecules) from gold. The observed rate (Fig. 3) from an initial coverage of 0.016×10^{15} atoms/cm² is about a factor of 10 lower than the clean-surface-adsorption rate at an atomic hydrogen pressure that gives this steady-state coverage (compare with Fig. 1).

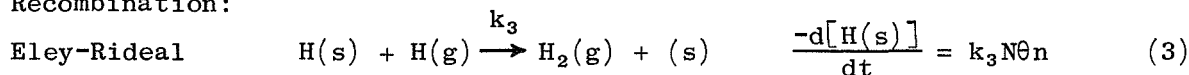
The observed characteristics of the atomic hydrogen-gold system are of particular interest because they can readily be interpreted in terms of the kinetics of the three elementary processes³ normally considered to be occurring at the surface. With this model we can then evaluate the relative importance of the two mechanisms of recombination. The following list associates these processes with mathematical expressions relating the rate of population or depopulation of hydrogen on the surface to the concentration of gaseous atoms, n , the surface number density of available adsorption sites, N , and the fraction of sites occupied by adatoms, θ .



Recombination:



Recombination:



Based on equilibrium data, the probability of atom desorption from gold is virtually nil, so we need not consider the reverse of reaction (1). In addition, under the conditions of our experiments, we do not observe sorption of hydrogen from the molecular state; hence, the reverse of reactions (2) and (3) is eliminated from our consideration.

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

$$k_1 N(1-\theta)n = k_2 (N\theta)^2 + k_3 N\theta n \quad (4)$$

Rearrangement of Eq. (4) gives a statement of the functional dependence of θ on n :

$$n = \frac{k_2 N\theta^2}{k_1(1-\theta) - k_3\theta} \quad (5)$$

The reaction rate constants (k_1 , k_2 , k_3) in Eq. (5) may be evaluated from our experimental rate data:

k_2 , obtained for the observed coverage from data in Fig. 3 using Eq. (2), $= 5.1 \times 10^{-16} \text{ (atoms/cm}^2\text{)}^{-1} \text{ min}^{-1}$;

k_1 , computed from data in Fig. 1 using Eq. (1), $= 1.25 \times 10^{-10} \text{ (atoms/cm}^3\text{)}^{-1} \text{ min}^{-1}$;

k_3 , obtained from Eq. (3), first computing the value of $k_3 N\theta n$, for the observed coverage using Eq. (4), $= 7.2 \times 10^{-9} \text{ (atoms/cm}^3\text{)}^{-1} \text{ min}^{-1}$.

The adsorption isotherm (θ vs n) obtained by solving Eq. (5) using these values of the rate constants, predicts a maximum steady-state surface coverage less than 0.02 monolayer as $n \rightarrow \infty$. This value is considerably smaller than the maximum observed in our experiments (Fig. 1). However, based on the observed relative flux of hydrogen atoms surviving transit through the reactor with the gold specimen,¹ it is evident that a significant fraction of the incident atoms do not recombine. Consequently, k_3 was adjusted to a lower value (2×10^{-9} (atoms/cm³)⁻¹ min⁻¹) to give an isotherm in reasonable agreement with the data (Fig. 4).

The relative values of the rate constants indicate that adsorption is the rate-limiting process in the recombination of hydrogen atoms on gold. This conclusion is further supported by the similarity in value of the recombination coefficient γ determined previously³ at a relatively high pressure ($P_H \cong 10^{-3}$ torr; $\gamma = 0.072$) and the clean-surface sticking coefficient ($S = 0.065$). We may compute k_3 from this value of γ on the basis of first order Eley-Rideal kinetics:³

$$k_3 = \frac{\gamma \bar{c}}{4N\theta}$$

where $\bar{c}$ is the mean atomic velocity. If we assume the high pressure limit of $\theta = 0.06$, this computation gives $k_3 = 4 \times 10^{-9}$, in reasonable agreement with the value derived from our low pressure rate measurements.

2. The Interaction of Oxygen Atoms and Hydrogen Atoms on Gold

The hydrogen atom concentration in the upper atmosphere is much smaller than that of oxygen atoms. This fact, considered together with the relatively high rate of adsorption of atomic oxygen on gold, suggests that one should be concerned with the rate and nature of the interaction between gaseous hydrogen atoms and oxygen adatoms.

We have investigated this reaction by means of the flash-filament technique. The gold ribbon specimen, flash cleaned, was exposed to a flux of atomic oxygen for a sufficient time to saturate the surface with a monolayer of adatoms. The oxygen supply to the system was then cut off, and, following a brief period of evacuation, hydrogen at a predetermined

constant flux was admitted to the atom source and the reactor for a period of time. After this exposure to hydrogen atoms, the hydrogen supply was interrupted and the ribbon was electrically heated to desorb residual adsorbed oxygen. Using our established technique,² we thus evaluated the mass of oxygen remaining on the gold surface after exposure to a constant flux of hydrogen atoms for various periods of time. The results, corrected for Langmuir-Hinshelwood oxygen atom recombination, are shown in Fig. 5. The initial rate, shown by the dashed line, is comparable to the incident flux of hydrogen atoms under the conditions of the experiment ($P_H \cong 5 \times 10^{-9}$ torr), and indicates that the reaction occurs with approximately unit efficiency. The products of the reaction could not be determined. A blank experiment, in which an oxygen-covered gold surface was exposed for 8 minutes to a flux of molecular hydrogen at $P_{H_2} \cong 10^{-6}$ torr, indicated that the rate of reaction of gaseous molecular hydrogen with oxygen adatoms on gold is negligibly small.

3. Experiments in a Reactor with Modified Geometry

To obtain quantitative values for the constants describing the solid surface/gas atom reactions, the gas flow equations describing flow through a cylindrical tube with apertures at either end and walls of variable reactivity must be solved. Unfortunately, solutions from our analytical model⁴ could be obtained only for geometries where the length and diameter of the cylinder are comparable. The use of such a geometry for our flash-filament adsorption experiments was impractical; hence most of our data was obtained in a reactor with a length/diameter ratio of 5.5/1.

To provide a direct empirical test of the analytical model, we carried out a selected set of experiments using a new reactor with dimensions similar to those of the model shown in Fig. 6. The reactor was fabricated from fused quartz. The diameter and length were each 5.1 cm ($L/D = 1$); the diameter of the entrance aperture was 0.6 cm whereas that of the exit aperture was 1.25 cm. All other components of the system were identical to those employed with the long reactor.²

The fraction of atomic oxygen in the outlet flux of the reactor was determined for the clean, empty reactor as a function of the temp-

erature of the tungsten atom source and the oxygen pressure at the source inlet. A second set of similar measurements was carried out after inserting in the reactor a silver foil liner, which covered exactly one-half the side wall of the reactor nearest the end containing the exit aperture (Fig. 6). This liner was cut from 0.010-in. silver foil, polished with a pure alumina abrasive, and washed thoroughly in distilled water. Rolled into a cylinder of slightly larger diameter than the reactor, it was held in place by spring tension. After evacuation, the silver was initially degassed by heating to approximately 300°C with a resistance heater surrounding the quartz reactor. Silver was chosen for this experiment because of its demonstrated⁵ indifference to carbon monoxide as a catalytic poison for oxygen-surface reactions. Consequently, we could be confident that it would exhibit its characteristic steady-state activity toward atomic oxygen without periodic flash cleaning.

The results of these experiments (Fig. 7) demonstrate a reasonably constant fractional diminution in the flux of oxygen atoms that survive transit through the reactor with the silver wall, over a range of source temperatures and pressures. The analytical model permits interpretation of this fractional loss in terms of a loss coefficient, α_{band} . The average observed value of relative exit flux, $n/n^* = 0.31$, corresponds to an overall loss coefficient, $\alpha_{\text{band}} \cong 0.1$ (Fig. 8), according to the analytical model. This value of loss coefficient is in reasonable agreement with our earlier measurements on the atomic oxygen-silver system, on the assumption that atom recombination by the Eley-Rideal mechanism is very slow. In these earlier experiments,⁶ the total atom loss rate at the silver surface by occlusion and Langmuir-Hinshelwood recombination was found to be approximately one-tenth the rate of impingement of gaseous atoms.

C. Practical Conclusions

1. The high efficiency of the reaction between gaseous hydrogen atoms and oxygen adatoms on gold observed in our experiments seems to be in conflict with reports of hydrogen atom number densities of the order of 10^8 cm^{-3} reported by the OGO-F satellite mass spectrometer at perigee.⁷

Since no ion fragments that could be attributed to water or to molecular hydrogen appear in the upper atmosphere mass spectrum, hydrogen atoms must survive transit through the sampling antechamber either as gaseous atoms or in some other combined form. We may speculate on two possible sources of hydrogen atoms.

a. Hydrogen atoms might react with surface sorbed oxygen to form the metastable radical OH. At 25°C, this species possesses a 9.4 kcal endothermic heat of formation,⁸ so its generation from its constituent atoms, even where one of them is in an adsorbed state, is thermodynamically quite favorable. Such radicals would undoubtedly dissociate after a few collisions with the wall. However, the products would be the constituent atoms, for the number density of adsorbed hydrogen is so low that an encounter with a hydrogen adatom to form water is highly unlikely. In contrast, the probability that the hydrogen atoms from collision-dissociated OH would react with another oxygen adatom is high, and we can conceive that a hydrogen atom could survive transit through the sampling antechamber by successive formation and dissociation of OH radicals. In the ion source of the mass spectrometer, the probability is high that nearly all the OH radicals ionized by electron impact would be fractured into H^+ and O^+ ions. Consequently only mass peaks at amu 1 and amu 16 would be observed. It has been reported⁷ that in the OGO-F mass spectrometer data, the intensity of the mass 16 peak demonstrates a slight increase in conjunction with increases of the mass 1 peak. This result, of course, is consistent with the proposed atom transport mechanism.

b. The source of the observed hydrogen might be nonatmospheric. It has been demonstrated⁹ that hydrogen diffuses readily through gold at temperatures as low as 100°C. Hence, hydrogen occluded in the gold plating on the mass spectrometer antechamber surface (or even hydrogen included in the stainless steel substrate) would diffuse to the free surface where, by reaction with an oxygen adatom, it would leave the surface as an OH radical.

By making a number of reasonable assumptions, we can estimate the concentration of hydrogen at the gold-plate/steel interface required to

maintain a steady-state number density of $H = 10^8 \text{ cm}^{-3}$ in the antechamber.

Our assumptions are:

- i) the gold surface is the sole source of hydrogen;
- ii) the rate of arrival of atoms by diffusion from the solid Ddn_s/dx is balanced by their departure through the antechamber inlet orifice with flux ϕ ;
- iii) the concentration n_s of $H(s)$ at the gold surface approaches zero;
- iv) the diffusive concentration gradient of atoms in the gold is linear;
- v) the thickness x of the gold-plate layer is 0.002 in. ($5 \times 10^{-3} \text{ cm}$).

From the dimensions of the antechamber and its orifice:⁷

$$\phi = Ddn_s/dx \cong 10^{11} \text{ atoms/sec.cm}^2 . \quad (6)$$

The diffusion coefficient D for hydrogen in gold at 25°C , obtained by extrapolation of available data,¹⁰ is $5 \times 10^{-8} \text{ cm}^2/\text{sec}$. Applying conditions iii, iv, and v to Eq. (6) gives a statement of the approximate value of the hydrogen concentration n_s at the gold-steel interface:

$$n_s \cong \frac{10^{11}x}{D} \cong 1.2 \times 10^{17} \frac{\text{atoms}}{\text{cm}^3} = 1.9 \times 10^{-7} \frac{\text{mole}}{\text{cm}^3} .$$

The molar density of gold at 25°C is $9.8 \times 10^{-2} \frac{\text{mole}}{\text{cm}^3}$. Hence, the computed value of n_s represents a fractional hydrogen content of $1.9 \times 10^{-7} / 9.8 \times 10^{-2}$ or $\sim 2 \text{ ppm}$. The presence of an occluded hydrogen concentration of this magnitude is quite plausible. Therefore, the solid surface of the mass spectrometer antechamber cannot be discounted as the source of the observed hydrogen ($\text{amu } 1$) peak. A critical analysis of the variation of $\text{amu } 1$ with altitude, relative to concurrent variations in $\text{amu } 16$, may provide further insight into the source of atomic hydrogen.

2. The apparent applicability of the analytical model to inter-

pretation of experimental data obtained in a short reactor ($L/D \cong 1$) suggests that solutions of the model for a long reactor geometry ($L/D \cong 6$) would be of great value in interpretation of data from the OGO-F mass spectrometer. The antechamber in this instrument possesses a length/diameter ratio $L/D \cong 6$. Consequently, refinement of this computational problem is considered to be of great importance to derive maximum practical benefit from the surface kinetic data obtained in this study.

D. Final Report

A Final Report summarizing the results of this project and discussing their significance is currently in preparation.

E. Personnel

Personnel participating in this project during the past quarter include Bill R. Baker, J. W. van Gastel, Henry Wise, and Bernard J. Wood.

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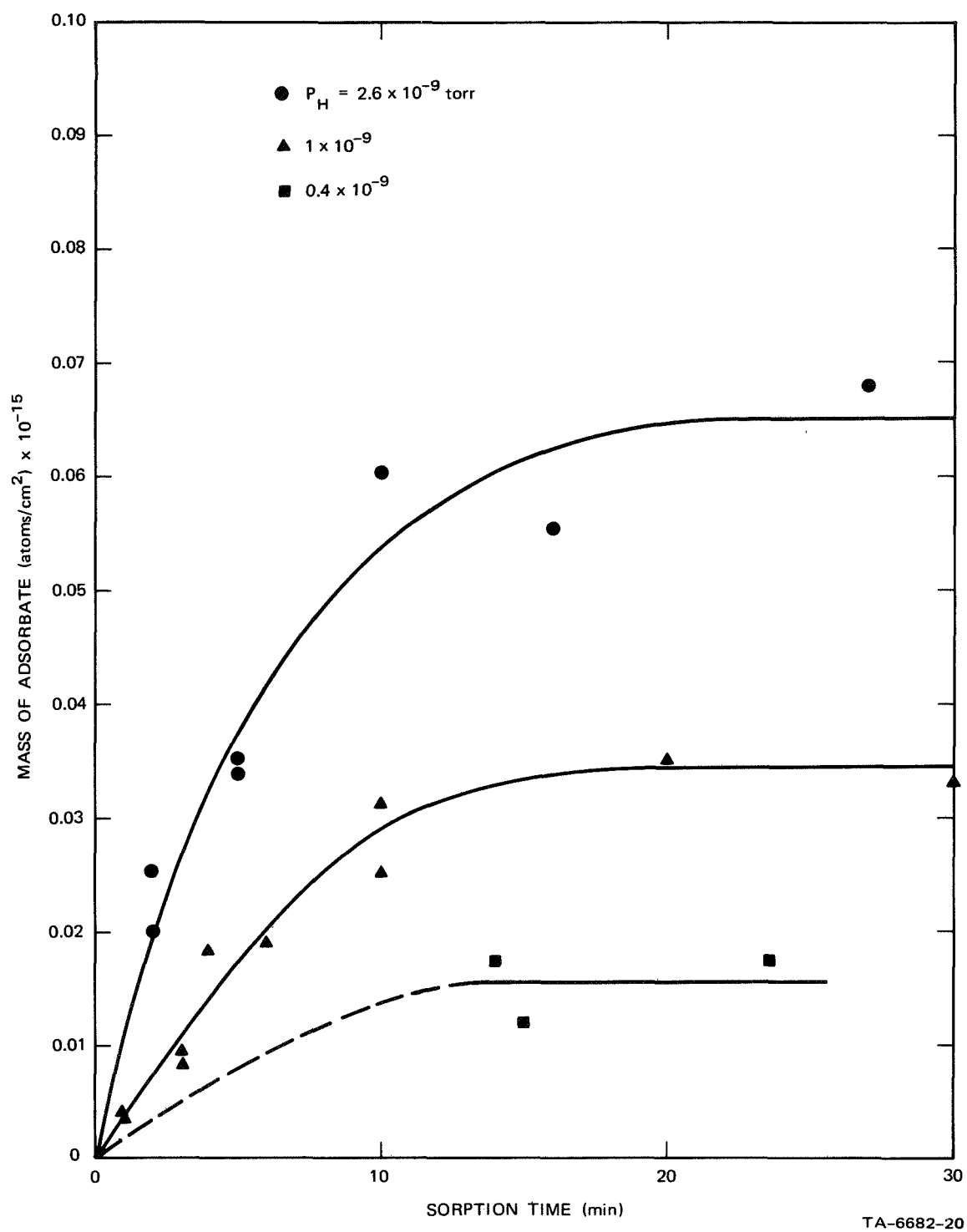
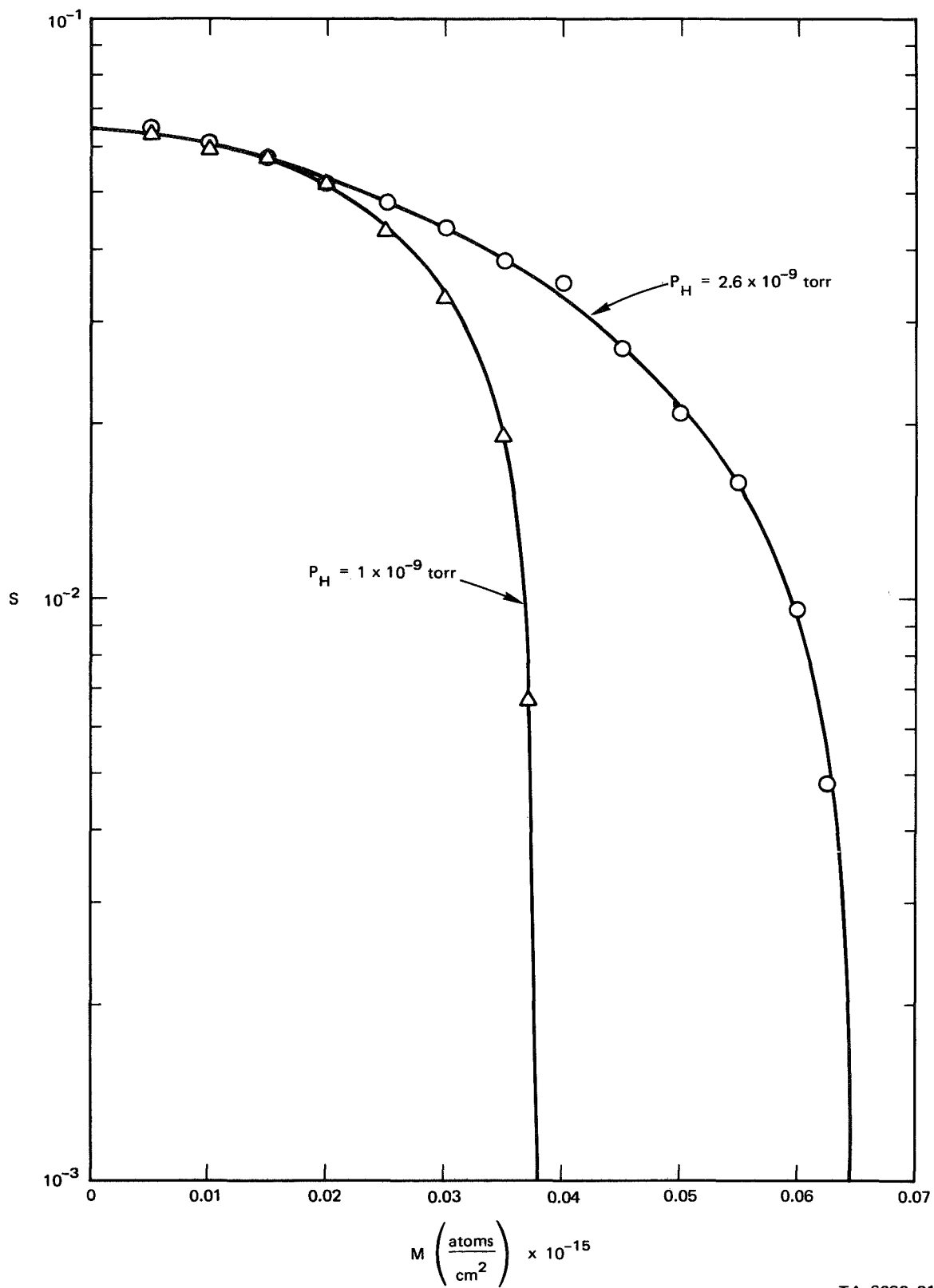


FIGURE 1 THE ADSORPTION OF ATOMIC HYDROGEN ON GOLD AT 25°C AS A FUNCTION OF PRESSURE.



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FIGURE 2 STICKING COEFFICIENT S OF ATOMIC HYDROGEN ON GOLD AT 25°C AS A FUNCTION OF SURFACE COVERAGE OF ADATOMS M . Points are normalized to coincide at $M = 0$ within precision of pressure measurements.

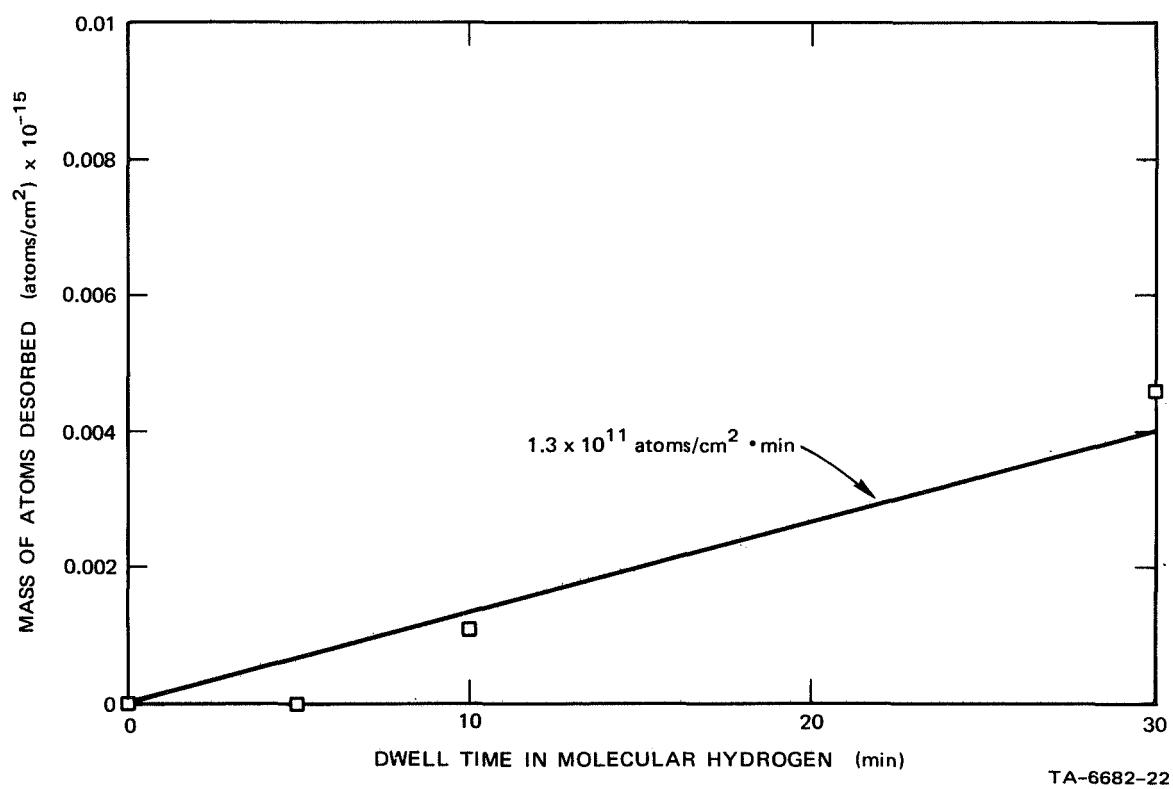
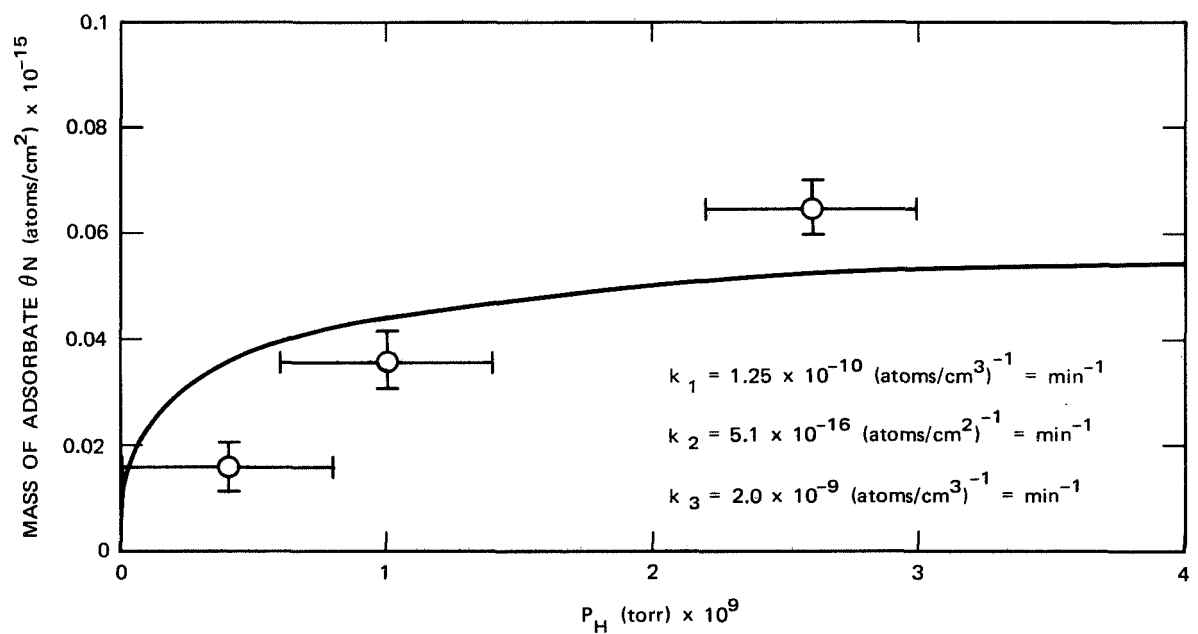


FIGURE 3 SPONTANEOUS DESORPTION OF HYDROGEN ADATOMS FROM GOLD AT 25°C. Initial coverage at time 0 = $0.016 \times 10^{15} \text{ atoms/cm}^2$.



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FIGURE 4 ISOTHERM FOR ATOMIC HYDROGEN ADSORPTION ON GOLD AT 25°C.
Curve computed from Eq. 5, using indicated values for rate constants;
experimental points from data in Figure 1.

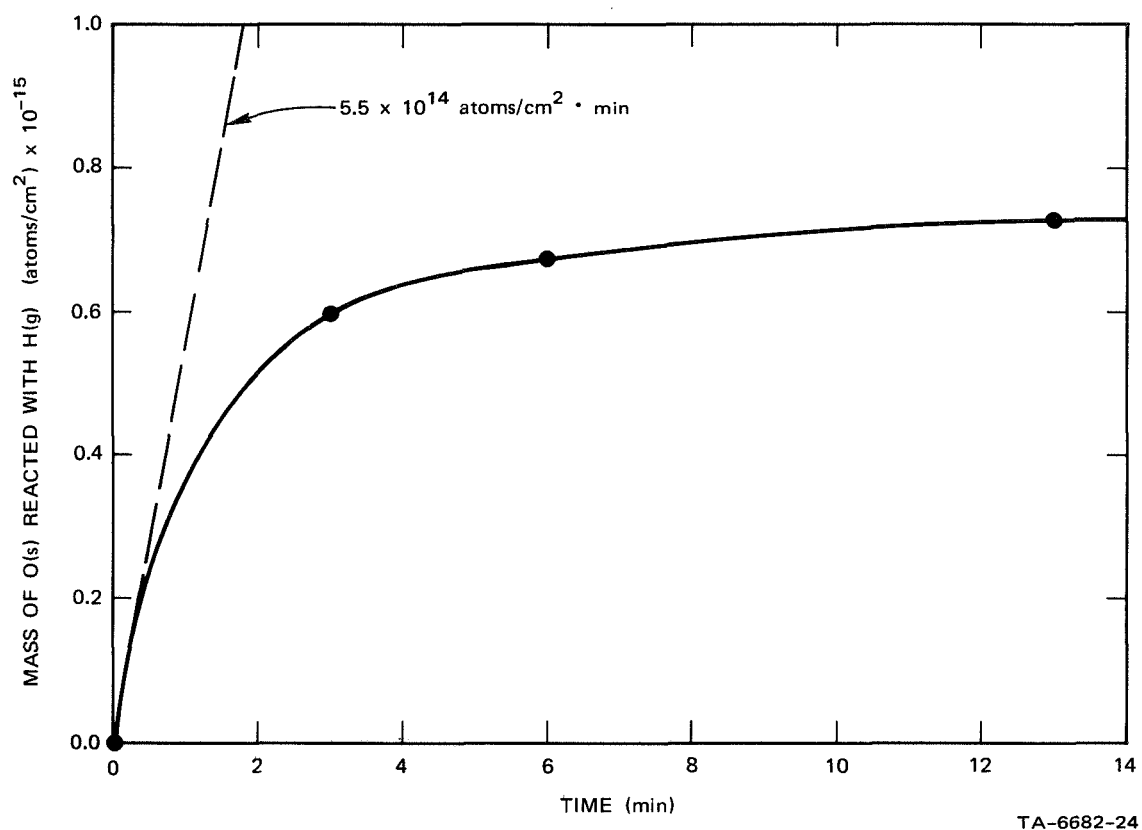
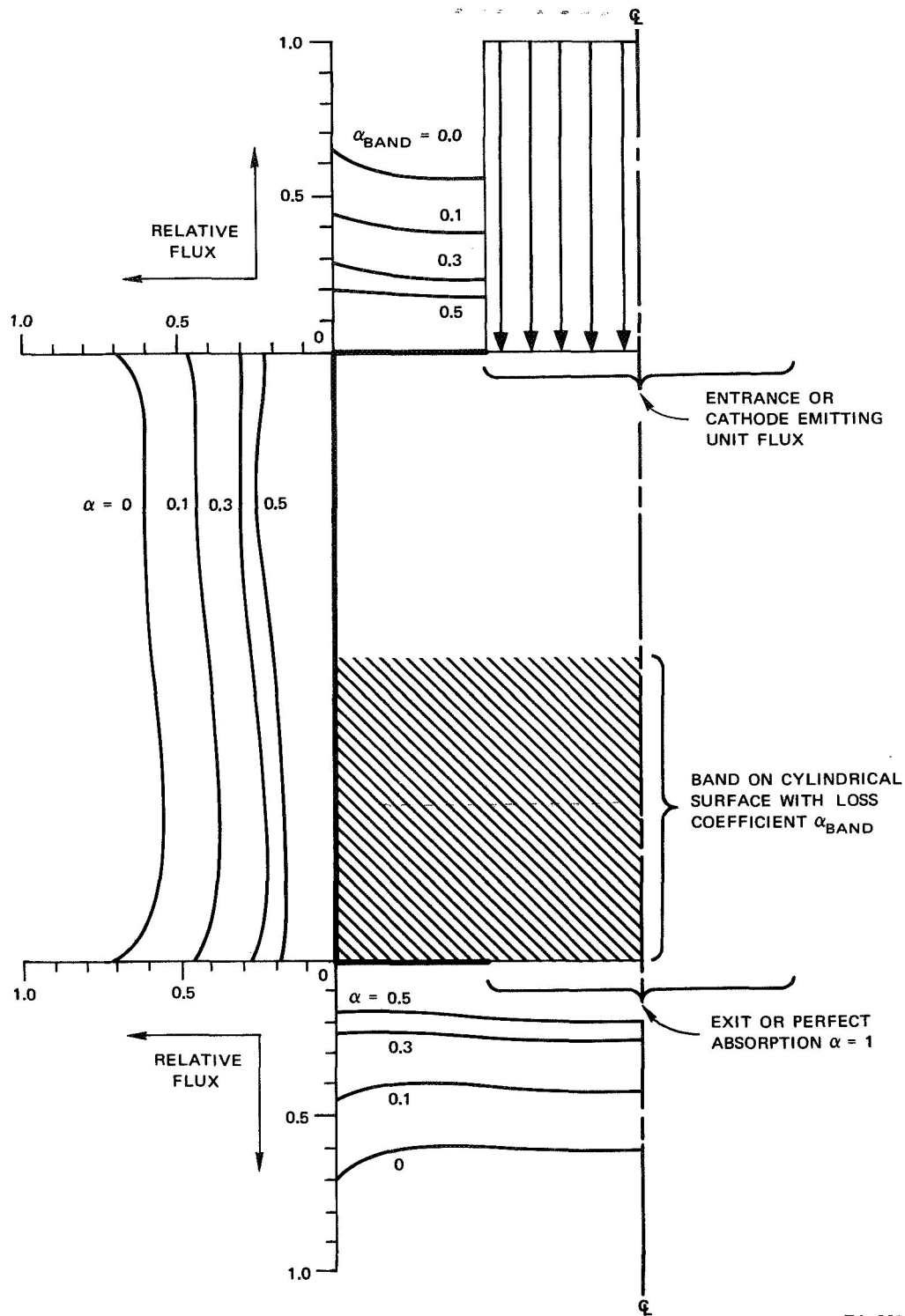
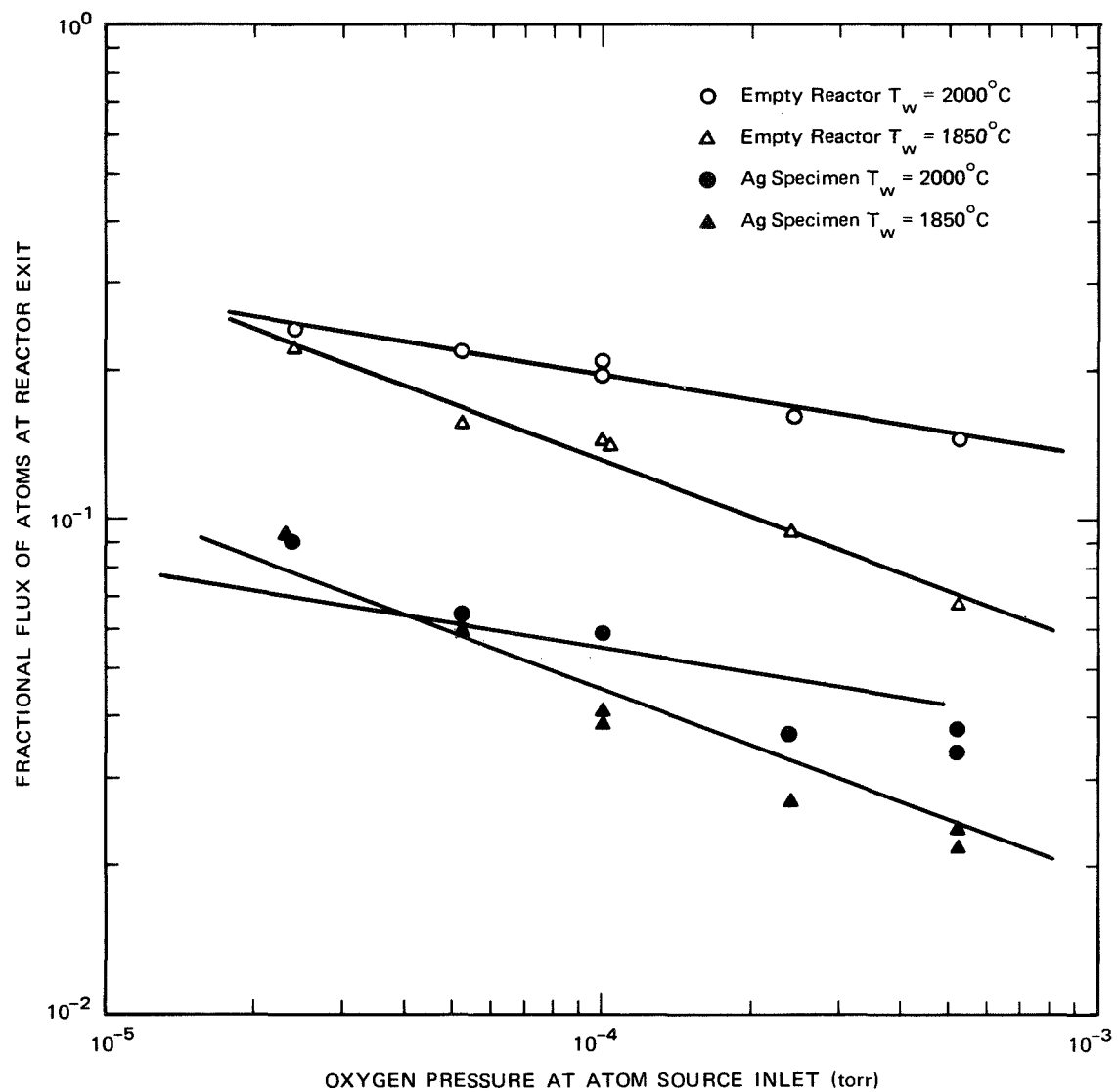


FIGURE 5 RATE OF REACTION OF GASEOUS ATOMIC HYDROGEN WITH OXYGEN ADATOMS ON GOLD AT 25°C. $P_H \cong 3 \times 10^{-9}$ torr. At time = 0, gold surface coverage with oxygen $\theta_N = 1.07 \times 10^{15}$ atoms/cm².



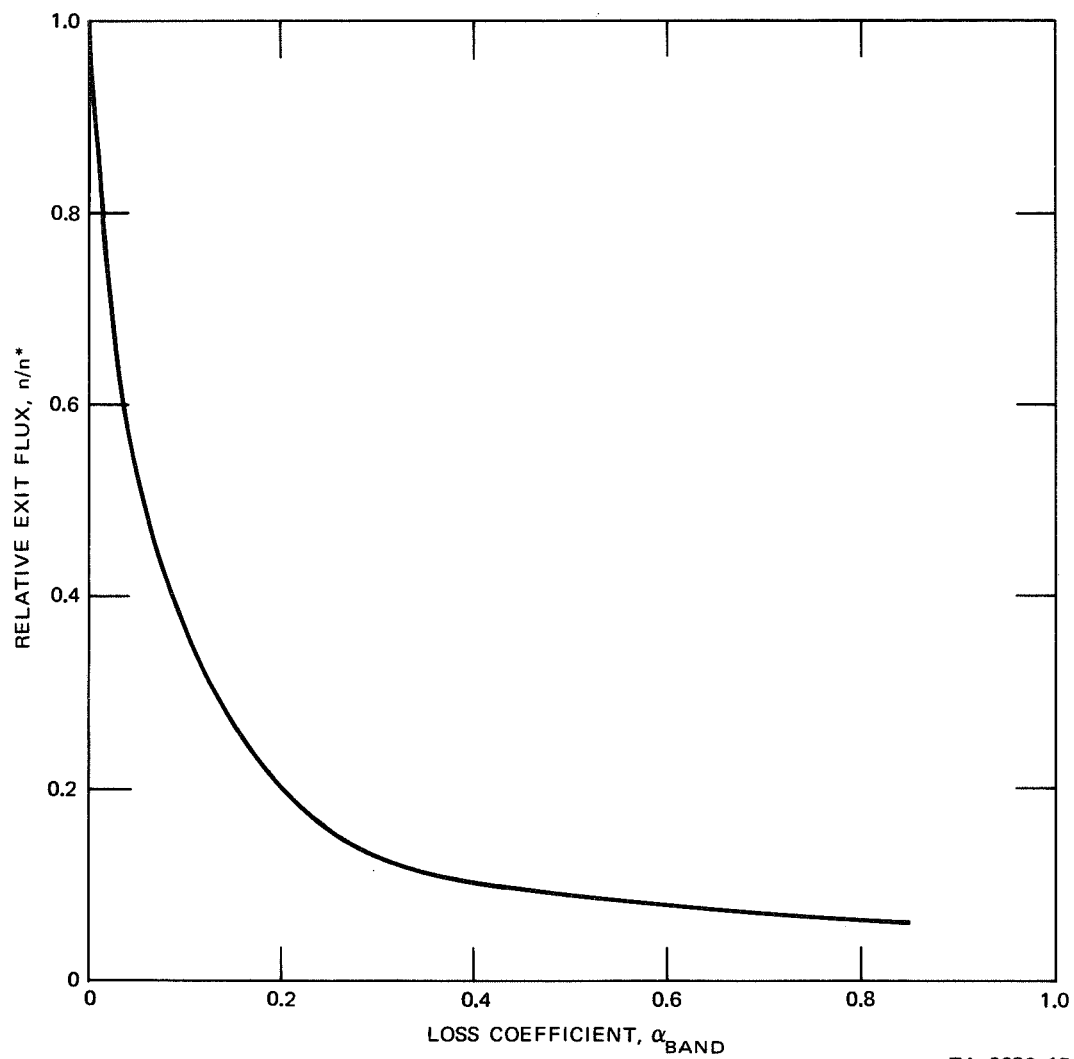
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FIGURE 6 LONGITUDINAL SECTION OF REACTOR MODEL SHOWING CALCULATED INTENSITY OF INCIDENT FLUX ON WALLS. The loss coefficient, α_{band} , is zero except on the half of the cylindrical surface nearest the exit, where $\alpha_{\text{band}} = 0, 0.1, 0.3, \text{ and } 0.5$.



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FIGURE 7 FRACTIONAL OXYGEN ATOM FLUX AT REACTOR EXIT AS A FUNCTION OF ATOM SOURCE TEMPERATURE, T_w , AND PRESSURE.



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FIGURE 8 DIMENSIONLESS TOTAL EXIT FLUX (REFERRED TO CASE OF $\alpha_{\text{BAND}} = 0$) AS FUNCTION OF α_{BAND} . Geometry is that depicted in Figure 6, except that exit aperture diameter corresponds to that employed in experimental reactor.