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

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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. 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 gold-foil and silver-foil specimens were described and discussed in Quarterly Status Reports No. 6 (December 1, 1968) and No. 7 (March 1, 1969).

## B. Experiments

### 1. Refinement of Analytical Model

The Need for a Better Model. The basis of our determination of the efficiency with which a metal surface removes impinging oxygen atoms from the gas phase is a measurement of the surviving flux of atoms at

the outlet of a reactor containing a specimen of the metal of interest.[1] An approximate model for such a system assumes a "stirred' reactor with negligible atom loss within the reactor in the absence of a metal specimen. Thus, no account is taken of the variation in atom population density from one end of the reactor to the other. Using this model one can compute a loss coefficient, $\Lambda$, based on the measured value of atom concentration at the outlet of the empty reactor, $n^*$, and that at the outlet of the specimen-containing reactor, n:

$$\Lambda = [(n^*/n) - 1]/\sigma \qquad (1)$$

In this expression $\sigma$ is the ratio of the specimen surface area $A_s$ to the corss sectional area of the reactor outlet aperture $A_e$. It is termed the effective collision number of the specimen.

This theoretical approach places no limitation on the geometric configuration of the specimen. In our experiments, therefore, we adopted a convenient arrangement which permitted flash-cleaning of the surface; namely, a long ribbon, suspended from electrical lead-throughs, which assumed a U-shape centered longitudinally about the axis of the reactor. Some discrepancy appeared in experiments with a silver specimen between the value of $\Lambda$ computed from Eq. 1 and that derived from sorption rate measurements.[2] This indicated a need to refine the analytical model to more closely approximate the physical arrangement of the experiment.

Development of a Better Model. Consideration of kinetic theory shows that in the molecular flow regime a finite concentration gradient exists within the cylindrical reactor so that only a fraction of the gas atoms entering the tube reach the outlet even in the absence of atom

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

[2]Quarterly Status Report No. 7, March 1, 1969

recombination on the reactor wall. The atoms which do not traverse the tube depart through the inlet, i.e., they are "reflected." There have been a number of theoretical approaches to such flow situations,[3] but all have treated the case of a straight tube of uniform cross section with no constricting apertures at either end. We have proceeded from this point with an analysis of molecular flow through a tube with apertures at either end and with walls exhibiting specified absorption efficiencies.

The model is depicted in Fig. 1. We make the fundamental assumption that atoms striking the walls are either absorbed with a probability $\alpha$ or are diffusely reflected with a spatial distribution density varying with the cosine law defined by the angle between the normal and the direction of departure. From this we can state an influence function which defines the fraction of atoms emitted from one element of surface incident on a second element, and vice versa. Three such influence functions are required. One, $\omega_{rr}$, defines atom transfer between elements on the opposite end plates of the reactor (ring-on-ring); the second, $\omega_{br}$, between elements on the end plates and those on the tube wall (ring-on-band); the third, $\omega_{bb}$, between different elements on the wall of the tube (band-on-band). If we define f as the flux density of atoms incident on a surface, then $(1-\alpha)f$ becomes the flux density of reflected atoms from that surface. For steady state, then, we may write a system of integral equations which describe the net flux of atoms at any point on the surface in the reactor as the summation over the surface elements of the product of the emitted flux and the appropriate influence functions. As a consequence of the geometry of the model, three equations

[3]See S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley & Sons, New York, Revised edition 1949, pp. 87-95.

are required: one for end 1 (Fig. 1):

$$f)\,r,o) = \int_{Z=o}^{L} \omega_{br}\,(r,Z)\;f(R,Z)\;[1-\alpha(R,Z)]\;2\pi R dZ$$

$$+\int_{o}^{R} \omega_{rr}\,(r,\rho,L)\;f\,(\rho,L)\;[1-\alpha(\rho,L)]\;2\pi\rho d\rho \qquad (2)$$

and for end 2 (Fig. 1):

$$f(r,L) = \int_{Z=o}^{L} \omega_{br}\,(r,L-Z)\;f(R,Z)\;[1-\alpha(R,Z)]2\pi R dZ$$

$$+\int_{o}^{R} \omega_{rr}\,(r,\rho,L)\,f(\rho,o)[1-\alpha(\rho,o)]\;2\pi\rho d\rho \qquad (3)$$

and a third for the tube wall (Fig. 1):

$$f(RZ) = \int_{z=o}^{L} \omega_{bb}\,(1z-\zeta 1)\,f(R,\zeta\,)\;[1-\alpha(R,\zeta\,)]\;2\pi R d\zeta$$

$$+\int_{o}^{R} \omega_{rb}\,(r,o)\,f(r,o[1-\alpha(r,o)]\;2\pi r dr$$

$$+\int_{o}^{R} \omega_{rb}\,(r,L)\,f(r,L)[1-\alpha(r,L)]\;2\pi r dr \qquad (4)$$

An outlet aperature of radius $r_2$ is accounted for in this model by setting $\alpha = 1$ for $o<r<r_2$ in end 2. The atom source, providing a flux

of constant density through an aperture of radius $r_1$ in end 1, is obtained by replacing $f(r,o)$ by a source function on the left-hand side of Eq. 2 for $o<r<r_1$, and in the second integrals of Eqs. 3 and 4. This system of equations can be solved by approximating the differentials with finite elements. The result is a linear system of algebraic equations which gives the average net flux density on any element of area.

A great advantage of this model is that the effective absorption probability $\alpha$ can be varied from point to point on the reactor surfaces to account for various specimen geometries employed in actual experiments. Computer programming and initial test computations are now in progress.

Application of the Model. The model accounts for atom removal only at the reactor wall or end plates. The relationship of a centrally-suspended metal specimen to one situated on the wall must be determined empirically. To do this we conducted experiments with wall liners of silver foil identical in source, pretreatment, and geometric surface area to the silver ribbon specimen used in earlier experiments.[2] By observing the atom flux at the outlet as the silver wall liner was moved from one end of the reactor to the other, we demonstrated that the atom loss coefficient for the two specimen geometries coincided when the wall liner was situated adjacent to the outlet end of the reactor. Hence, we shall be able to reinterpret the extensive data we have already obtained from suspended ribbon specimens, and make use of this convenient geometry for further experiments with full confidence that they can be interpreted by the new analytical model.

## 2. Measurements with Titanium Specimen

A ribbon, cut from type 75A commercially pure 0.001″ titanium foil,[4]

[4]Manufacturers impurity analysis: 0.05% C; 0.006% $H_2$; 0.31% $O_2$; 0.010% $N_2$; 0.21% Fe.

was mounted in the reactor. In every other respect the apparatus was identical to that described in preceding reports.[5] The quadrupole mass analyzer was calibrated before and after each experiment in the manner previously described.[5]

Before exposing the titanium specimen to atomic oxygen, the ribbon was annealed at temperatures up to 900°C and degassed under high vacuum conditions. During this treatment large quantities of hydrogen and water were observed flowing out of the reactor. CO and $CO_2$ were also noted but in considerably smaller quantities (less than 1% of the $H_2$). Upon continued heating at 550°C, the water, CO, and $CO_2$ diminished quite rapidly relative to the hydrogen, which required several hours to reduce to less than 10% of its original value.

Following this treatment, the ribbon, at 25°C, was exposed to a flux of atomic oxygen from the tungsten ribbon source at the reactor inlet. No flux of oxygen atoms was observed at the reactor outlet, and this situation persisted during the approximately hour-long duration of this experiment (Table I).

After evacuating the reactor to base pressure ($\sim 10^{-9}$ torr) the specimen was heated to 750°C. As before, water and hydrogen were the major components liberated; no atomic oxygen was observed.

The specimen was then deliberately oxidized by heating to 750°C in molecular oxygen at $P \cong 10^{-6}$ torr for a period of 105 minutes. During this time the steady-state oxygen pressure diminished, rapidly at first, then more slowly. When the ribbon was cooled, the oxygen pressure rose to its original value within a few minutes. The specimen exhibited no dramatic change in appearance; it was still a satin silvery grey in color, as it had been originally.

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[5]Quarterly Status Report No. 6, December 1, 1968.

A repeat of the atomic oxygen exposure experiment now gave significantly different results. A substantial fraction of the incident atomic oxygen appeared at the outlet of the reactor (Table 1). Based on the simplified theory, we computed the value of the atom loss coefficient to be $\Lambda = 0.03$.

When the specimen was heated under these conditions, the picture changed dramatically (Fig. 2). At a specimen temperature of 500°C, both atomic and molecular oxygen diminish but the former much less so than the latter. The molecular oxygen reaction rate changes with time in such a way that the pressure of $O_2$ increases until a new steady state is attained. Cooling the titanium restores the molecular oxygen nearly to its original pressure, but the atomic oxygen pressure remains at a reduced value (Fig. 2).

Finally a subsequent experiment carried out in pure molecular oxygen showed no change in the ratio AMU16/AMU32 with titanium specimen temperature, and very little affinity for molecular oxygen. However, the ribbon had now acquired a distinct blue coloration, presumably an oxide film of some thickness.

## C. Discussion

The behavior of titanium in the presence of atomic and molecular oxygen is complex. It seems likely that the complexity may be related to variations in the surface composition of the specimen. At least four oxides of titanium, viz., TiO, $Ti_2O_3$, $Ti_3O_5$, and $TiO_2$, have been characterized and are known to be highly stable compounds, even at molecular oxygen pressures less than $10^{-8}$ torr. In addition, there undoubtedly exist nonstoichiometric titanium-oxygen combinations which may exhibit varying degrees of stability relative to the stoichiometric oxides. In one study[6] it was established that titanium reacted initially with oxygen

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[6]P. Kofstad: J. Less-Common Metals, 12, 449 (1967).

at low pressures by dissolution of the gas into the metal lattice. The rather dramatic initial enhancement in the affinity of the metal for molecular oxygen versus atomic oxygen upon heating (Fig. 2) may be caused by a significant difference in the energies of activation for molecular oxygen dissolution compared to atomic oxygen dissolution. The activation energy value for the former process has been reported[4] to be 22 kcal/mole, while one would expect the latter process to be virtually nonactivated.[5] Hence, though the rate of interaction of titanium with molecular oxygen may be substantially slower than with atomic oxygen at 25°C, the situation may be reversed at 500°C. Also the high concentration of $O_2$ relative to O contributes to the observed difference in reaction rate.

The high reactivity of the vacuum annealed specimen for atomic oxygen we attribute to a relatively clean metallic surface. The appearance of water and hydrogen during the annealing process suggests that oxides on the surface may have been reduced by this treatment, leaving clean titanium with a very high affinity for atomic oxygen. Conceivably, long exposure of this surface to the atomic oxygen atmosphere would have passivated it.

## D. Practical Conclusions

(1) The complex behavior of titanium in the presenceof atomic and molecular oxygen prompts us to conclude that use of this metal in or near the sampling chamber of a flight mass spectrometer requires passivation of the metal surface by pretreatment with oxygen. But the conditions under which such a passivated surface will be stable are not clearly established and may be difficult to attain in the upper atmosphere. As a result, variation in activity with exposure time is to be expected.

(2) The new theoretical model may be of direct value in interpreting the atomic oxygen data reported by the OGO-F satellite mass spectrometer, because the configuration of the sampling antechamber in this instrument is cylindrical. Some corrections may be required due to the position of the outlet aperture on the side of the cylinder. This question will be pursued in our future work.

## E. Future Work

Our immediate plans are twofold. (1) We shall complete the work on the analytical model and apply it to the experimental data we have accumulated. (2) Experimental measurements on the metals of greatest interest, viz., gold and silver, will be continued using electroplated and/or evaporated films instead of foils for specimens.

## F. Personnel

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

Table 1

EFFECT OF TITANIUM SPECIMEN ON GAS COMPOSITION AT REACTOR OUTLET

| Specimen | | Flux* at Reactor Outlet (torr-l/sec x $10^6$ | |
|---|---|---|---|
| Temperature ($^oC$) | Pretreatment | O | $O_2$ |
| 25 | Vacuum anneal | 0 | 22.7 |
| 25 | Oxidation | 0.615 | 21.2 |
| 500 | Oxidation | 0.27 | 4.2 |
| empty reactor | | 0.98 | 21.3 |

*Steady state values obtained with inlet pressure 1 x $10^{-4}$ torr and tungsten atom source at 2000$^o$C. All values for O corrected for mass spectrometer cracking factor.

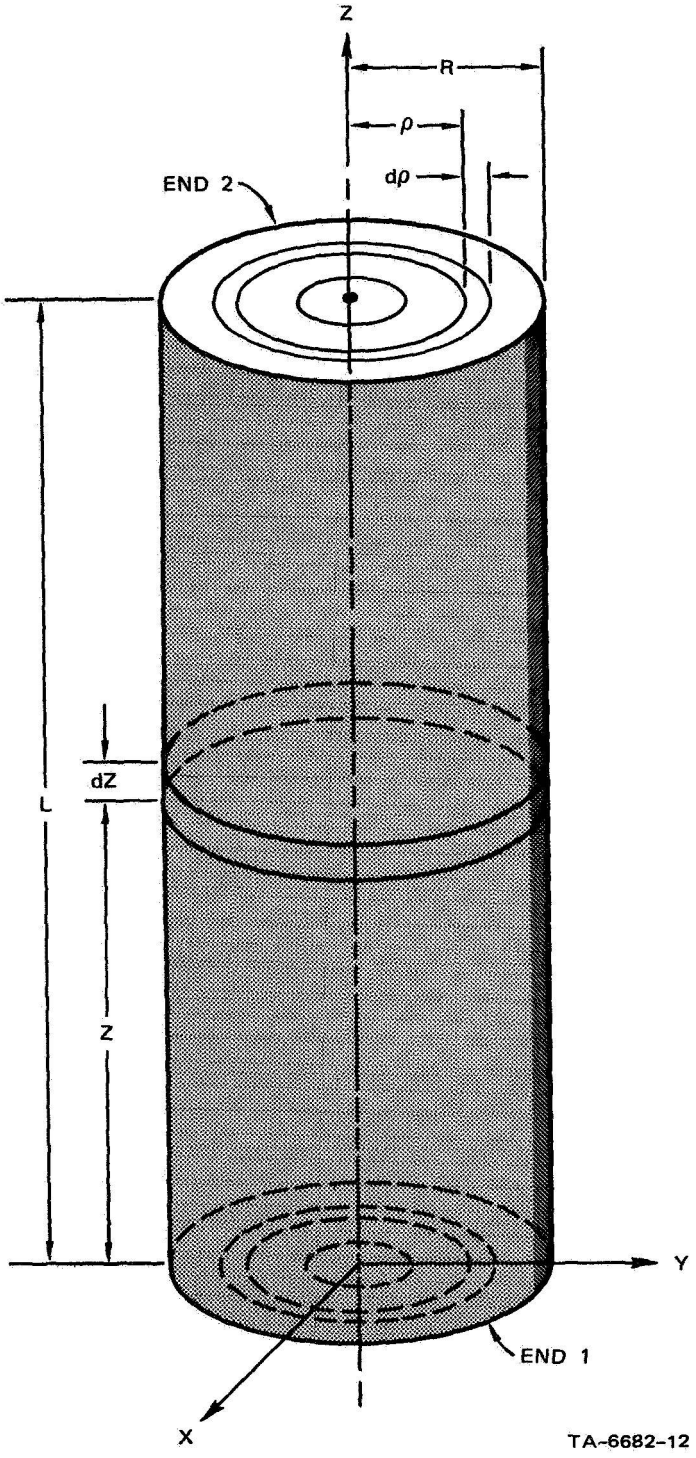


FIGURE 1 REACTOR MODEL

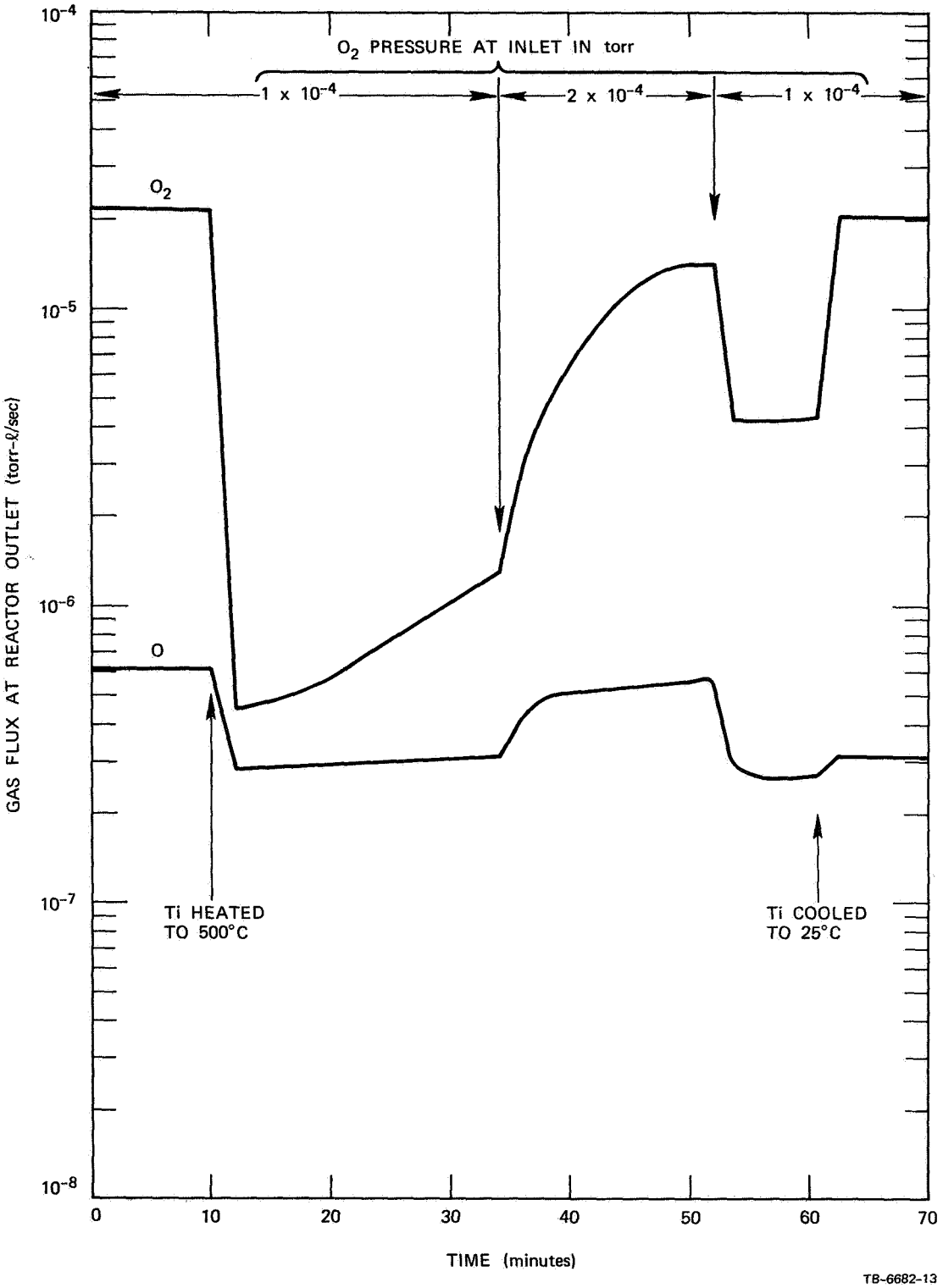


FIGURE 2 EFFECT OF TITANIUM SPECIMEN TEMPERATURE ON GAS COMPOSITION AT REACTOR OUTLET