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

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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 various 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 in order to allow quantitative interpretation of the mass spectrometer signal in terms of the composition of the upper atmosphere.

To minimize the problem of atom loss caused by heterogeneous atom reaction outside the sampling chamber in the laboratory experiment, we have utilized an experimental approach in which changes in total gas pressure and oxygen atom production rate are held nearly constant. The theoretical basis for the experiment was described in detail in Quarterly Status Report No. 1 (September 1, 1967). Subsequent experiments with molecular oxygen, reported in Quarterly Status Report No. 2 (December 1, 1967), verified the general validity of the approach for measuring low-pressure gas-surface interaction kinetics. The contribution of catalytic processes other than simple atom sorption or recombination, revealed by an examination of the oxygen-carbon monoxide-platinum system, was discussed in Quarterly Status Report No. 3 (March 1, 1968). Difficulty in obtaining measurable steady-state concentrations of atomic oxygen in the original apparatus, however, led to the design of a new system described in detail in Quarterly Status Report No. 4 (June 1, 1968).

Experiments

Analytical Basis

The experimental apparatus (Fig. 1) consists of a cylindrical

reaction vessel through which oxygen atoms flow from a source at one end to a high-capacity vacuum pump at the opposite end. Under the conditions of molecular flow, which apply throughout the pressure range 10^{-6} - 10^{-9} torr employed in this apparatus, simple kinetic theory suggests that once an atom enters the reactor it will depart through the exit aperture after suffering multiple collisions with the reactor wall. However, if the atom recombines with another atom during one of these collisions, it will leave the reactor as an oxygen molecule.

The following analysis is based on the assumptions that (a) the atom density represents a small fraction of the total gas concentration and (b) surface reactions are first order with respects to gaseous atoms. The rate of change in atom density n_1 inside the reactor of volume V is given by the difference between the number entering per second Q_1 and the sum of (a) the number leaving through the exit aperture of area A_e and (b) the number reacted by interaction with the surface of area A_R :

$$\frac{dn_1}{dt} = \frac{Q_1}{V} - \frac{n_1 \bar{c}}{4} (A_e + \gamma A_R) \quad (1)$$

where $\bar{c}$ is the mean atomic velocity and γ the probability of a reactive collision. Under steady-state conditions

$$n_1 = \frac{4Q_1}{\bar{c}V} [1/(A_e + \gamma A_R)] \quad (2)$$

For a reactor whose surface activity is so low that $\gamma = 0$ (perfect reflector)

$$n_1^* = 4Q_1/\bar{c}VA_e \quad (3)$$

Thus the ratio in atom density for these two reactors is given by

$$n_1/n_1^* = A_e/(A_e + \gamma A_R) = 1/[1 + (\gamma A_R/A_e)] \quad (4)$$

or

$$n_1/n_1^* \approx 1/(1 + \gamma\sigma) \quad (5)$$

where $\sigma \equiv A_R/A_e$ represents the average collision number, i.e. the average number of collisions made by each incoming atom with the reactor wall.

A reactor of very low surface activity is obtained by using Pyrex glass which has a recombination coefficient of $\sim 10^{-4}$. Hence, Eq. 5 is applicable for the evaluation of recombination efficiencies of metals by measurement of the effective atom concentration ratio observed in our apparatus when the various metals are placed in the reactor.

It is of interest to note that the magnitude of the ratio n_1/n_1^* is independent of the absolute value of atom concentration in the reactor (Q_1 constant). However, if atom recombination occurred as a result of a second order mechanism, an atom concentration term would appear in the denominator on the right-hand side of Eq. 5, and the value of n_1/n_1^* would diminish with increasing atom concentration. This characteristic of the system makes it possible to determine the order of the process by which atoms are removed within the reactor.

Apparatus and Procedure

Our reactor (Fig. 1) is a Pyrex cylinder with an inside diameter of 2.2 cm and a length of 10 cm. Atoms are generated by thermal dissociation of molecular oxygen on a tungsten ribbon in a water-cooled chamber at the lower end of the reactor. The reactor inlet is a 0.32-cm-radius aperture in a glass plate situated in close proximity to the tungsten ribbon. The reactor outlet is a 0.55-cm-radius aperture in a glass plate which leads directly to a large chamber pumped to low pressure by a titanium sublimation pump and an ion-getter pump. This chamber contains a quadrupole mass spectrometer situated in such a way that its ion source is immediately adjacent to the reactor exit aperture. The mass spectrometer thus analyzes the relative composition of the gas in the reactor, specifically,

the ratio of oxygen molecules to oxygen atoms. The total pressure in the system is determined by ion gages near the inlet and on the analyzer chamber, and can be controlled by adjusting the leak rate of O_2 into the system. The temperature of the tungsten ribbon, and thus the inlet atom flux, can be varied by adjusting the heating current.

Metal surfaces can be introduced to the reactor either as cylindrical inserts--foils or evaporated films--or as ribbons connected to electrical lead-throughs which permit flash cleaning of the specimens by electrical resistance heating.

Results

1. Pyrex Reactor

The ratio of atomic to molecular oxygen in the empty reactor was evaluated as a function of the total pressure of molecular oxygen and the temperature of the tungsten ribbon. The results are shown in Table I.

2. Gold Foil Specimen

A strip of 0.002-inch-thick gold foil with a total geometric surface area of 24 cm^2 was supported in the reactor by means of the electrical lead-throughs. Conditions of pressure and tungsten ribbon temperature similar to those employed in the experiments with the empty reactor were duplicated. Based on the measured fractions of surviving atoms, values of recombination efficiency for gold were calculated using Eq. 5 (see Table II).

It was noted in these experiments that the catalytic activity of the gold appeared to increase with exposure to atoms. This time variation is shown in Table III.

Discussion

The close correspondence between the fraction of atoms observed to survive the transit through our 80-collision Pyrex reactor, and the

fractional atom flux expected to appear from the hot tungsten surface at the inlet of the reactor (based on the kinetics of molecular oxygen dissociation on tungsten¹) suggests that the recombination efficiency of Pyrex is low. If the ratio n_1/n_1^* in an 80-collision vessel has a value of 0.99 (where n_1^* represents a vessel with zero recombination efficiency and n_1 represents the Pyrex vessel) then Eq. 5 predicts $\gamma = 1.3 \times 10^{-4}$ for the Pyrex wall. This is in agreement with the recombination efficiency reported for oxygen atoms on Pyrex at considerably higher oxygen pressures.² With such a low catalytic activity, the loss of atoms on the glass wall may be ignored, and the recombination efficiency of metal surfaces inserted in the reactor may be computed from Eq. 5, using for n_1^* the concentration of surviving atoms observed in the empty reactor under similar conditions of temperature and oxygen pressure.

Gold appears to be a relatively active oxygen recombination catalyst. The data in Table II suggest that the recombination rate has a higher than first order dependence on the gaseous atom concentration, for as the tungsten ribbon temperature is increased, the recombination efficiency increases. However, gold also exhibits an increasing activity with exposure to oxygen atoms (Table III). During a period of 35 minutes the observed recombination efficiency of the gold specimen increased about four-fold. It seems possible that this effect may be responsible for the apparent kinetic dependence. Further experiments will be conducted to clarify this point.

In a few experiments, the gold specimen which had been exposed to atomic oxygen for various lengths of time was flash heated and the amount of desorbed molecular oxygen observed. These results indicated that the

¹P. O. Schissel and O. C. Trulson, J. Chem. Phys., 43, 737 (1965).

²H. Wise and B. J. Wood, Advances in Atomic and Molecular Physics, New York, Academic Press, 1967, p. 322.

oxygen was sorbed relatively slowly, requiring more than 10 minutes to approach a saturated condition. Such a rate of accumulation of sorbed oxygen on the gold surface is in agreement with the observed change in recombination efficiency upon exposure to gaseous atoms.

Both in geometry and dimensions, the antechamber that comprises the gas inlet to the ion source of the OGO-F Satellite mass spectrometer is quite similar to our laboratory reaction vessel. Based on the analysis employed in our experiments, we can specify the recombination efficiency requirement for the surfaces of this antechamber for any specified recovery of oxygen atoms entering its inlet aperture. If 90 percent of the entering atoms must survive passage through the chamber ($n_1/n_1^* = 0.9$) then, from Eq. 5, the recombination efficiency γ cannot exceed 4×10^{-3} (the collision number σ of the antechamber is approximately 25). It seems evident that gold is not the surface of choice for this chamber. However, if gold is employed, it will be important to have a thorough knowledge of the recombination efficiency of this metal as a function of the gaseous atom concentration, the time of exposure, the total pressure, and, possibly, the temperature of the surface.

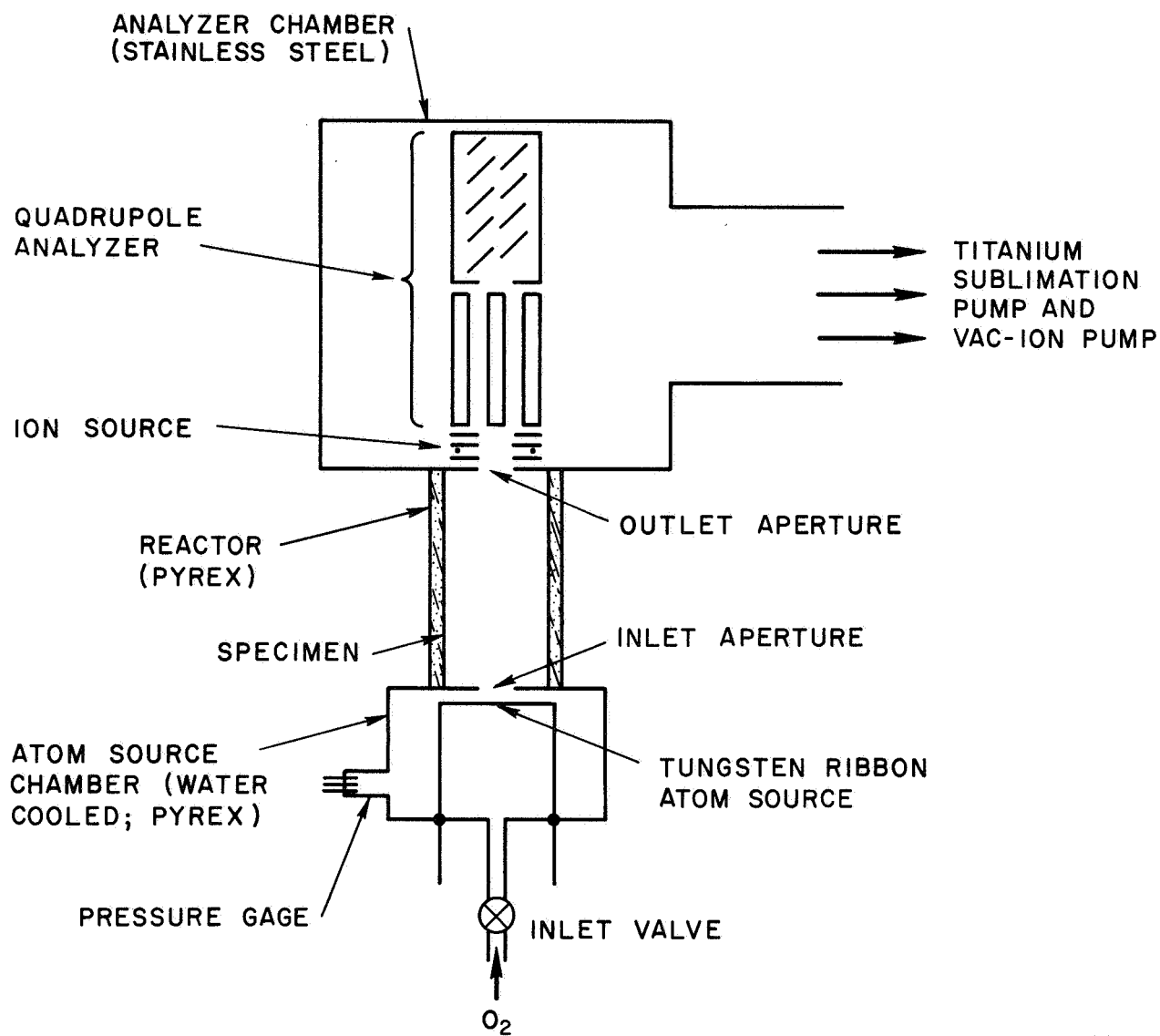
Our immediate future plans are to complete the measurements on gold, and then to pursue similar measurements on other metals. Materials of special interest at present are titanium, stainless steel, and aluminum.

Meeting and Trips

Henry Wise and Bernard J. Wood participated in the Conference on Atomic Oxygen Measurements in the Earth's Upper Atmosphere held at Goddard Space Flight Center on August. 7.

Personnel

Personnel participating in this project include Henry Wise and Bernard J. Wood.



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FIG. 1 SCHEMATIC DIAGRAM OF APPARATUS. Specimen may be film deposited on wall of reactor (as shown) or metal ribbon suspended inside reactor (not shown).

Table I

PRODUCTION OF ATOMIC OXYGEN ON A HOT TUNGSTEN RIBBON

Ribbon Temperature, °K	P_{O_2} , torr x 10^6	amu 16/amu 32	
		Observed ^a	Computed ^b
2150	0.51	0.20	0.30
--	1.5	0.13	0.17
--	5.0	0.10	0.096
2350	0.35	0.26	0.26
--	1.2	0.19	0.16
--	4.4	0.14	0.12

^a amu 16 was corrected for contribution of cracking pattern which was observed when the ribbon was not heated.

^b Computed from data in Ref. 1.

Table II

RECOMBINATION EFFICIENCY OF OXYGEN ATOMS ON GOLD

Ribbon Temperature, °K	Recombination Efficiency, γ
2150	0.084
2350	0.11
	0.16

Table III

EFFECT OF EXPOSURE TIME ON RECOMBINATION EFFICIENCY OF GOLD

Time of Exposure to Atoms, (minutes)	Recombination Efficiency, γ
0	0.065
5	0.21
20	0.27
35	0.27