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Lawrence R. Thorne

Utah State University

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OXIDATION OF THIN SILVER FILMS BY OZONE AND ATOMIC OXYGEN

by

Lawrence R. Thorne

An honors thesis submitted in partial fulfillment
for the requirements for the degree

of

BACHELOR OF SCIENCE

in

CHEMISTRY
(Honors Section)

Approved:

Utah State University
Logan, Utah
1973

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Also, the meticulous work of Adrian Blau in constructing much of the glass flow system was invaluable.

Lawrence R. Thorne

ABSTRACT

Recently, thin silver film detectors have been used to determine atomic oxygen profiles in the 70-100 km region of the upper atmosphere. The detectors' sensitivity to atomic oxygen is the result of the formation of silver oxide(s) which cause their electrical resistance to increase. A common procedure to calibrate and to make these detectors more sensitive is to cycle them through a series of three or more oxidations and reductions. This paper indicates that this cycling makes silver films more sensitive to ozone, causing them to be usable only at heights greater than 38 km. Also reported herein are experimentally determined sticking coefficients for atomic oxygen and ozone on a cycled silver surface as being 2.8×10^{-2} and 5×10^{-5}, respectively.

In an attempt to understand better the nature of the oxidation of silver by ozone and atomic oxygen, the proposed kinetics of these two reactions are reviewed, and supporting evidence for a previously proposed model reported.

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INTRODUCTION

One of the most important measurements in the study of the earth's atmosphere is the determination of atomic oxygen densities in the 70 to 100 km region. It is of particular interest since huge amounts of high-energy solar radiation are deposited in this region via a chemical process which produces atomic oxygen. To date, measurement of atomic oxygen density profiles has been difficult. Attempts have been made using mass spectrometers, nitric oxide releases, photometers, and catalytic recombination devices. Recently a most promising technique has been developed which makes use of the fact that the electrical resistance of thin silver films increases as they react with atomic oxygen. This paper discusses some of the chemical properties of these detectors.

THEORY AND BACKGROUND

Oxidation of Silver by Several Allotropic Forms of Oxygen

The Oxides of Silver

There are two known oxide forms of silver: Ag_2O and AgO, the former being the most common. The silver in Ag_2O displays the common +1 oxidation state as it is covalently bound to oxygen through sp-coordination (McMillan, 1960). The crystalline structure is cubic (Weast, 1967).

By its diamagnetic behavior (McMillan, 1960) and neutron diffraction (Scatturin, Bellon and Salking, 1961), AgO was found not to be a true bivalent silver oxide, but $Ag(I)Ag(III)O_2$. The Ag(1) are bound to O's by sp-coordination and the Ag(III) are bound by dp-coordination to the two closer of its four nearest oxygen atoms and by sp-coordination to the other two. This gives an overall hybridization of dsp^2. Servian and Buenafama (1969) have shown the existence of Ag(III) chemically. $(AgO)_2$ is a strong oxidizer and can transfer O to unoxidized silver which underlies it in a silver film (Thomas and Baker, 1971).

Gas-Solid Interface

Since silver strongly adsorbs O_2 it would be well to comment on the silver-gas interface. Figure 1 shows the potential energy curves for various types of adsorption. Curve A shows the simplest consideration, that is, physical absorption by van der Waal's forces only. In the second case a molecule may be dissociated and chemisorbed (curve B) by overcoming the potential barrier at P. Curves C and D refer to atom recombination in the discussion which follows.

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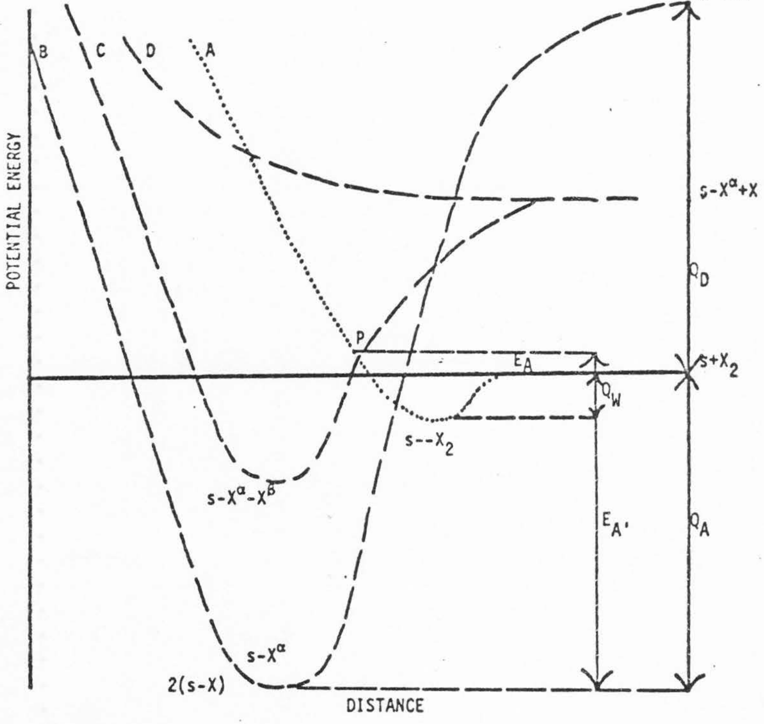
[1] In general "thin silver film" will refer to films, vacuum deposited 50-250 Å in thickness.

Figure 1

ENERGY DIAGRAM FOR SURFACE INTERACTION

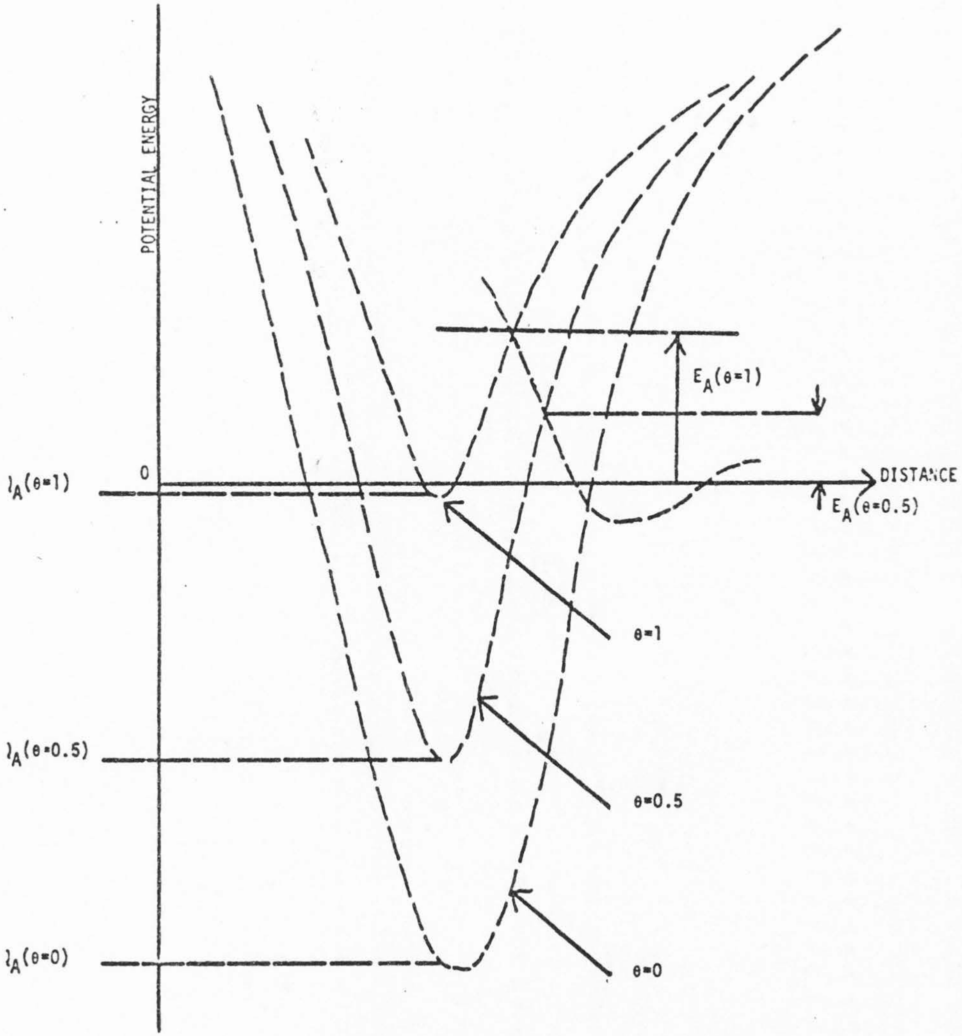


s = surface site
X = an atom
s-X = an absorbed atom
Q_D = dissociation energy of a molecule X_2
Q_A = absorption energy for two atoms
E_A = activation absorbed
Curve A = physical absorption of a molecule
Curve B = chemisorption of atoms
Curves C & D = atom recombination

(after Wise and Wood 1967)

Figure 2

FORMAL REPRESENTATION OF THE DEPENDENCE OF THE ACTIVATION ENERGY, E_A, ON THE FRACTION OF THE SURFACE COVERED, θ.



(after Bond 1962)

Bond (1962) (Figure 2) indicates that as the fraction (θ) of surface sites occupied increases, the adsorption potential energy curve changes. In general, as the surface becomes covered, the activation energy (E_a) increases. Imre (1968) indicates that adsorbed O_2 may exist in two states, parallel and perpendicular to the surface. Hence, Figures 1 and 2 are oversimplifications.

Oxidation by Molecular Oxygen (O_2)

Even though silver strongly adsorbs O_2, no oxidation takes place at room temperature. Bennett (1969) found no trace of silver oxide while examining tarnish on silver films. Czanderna (1964) found pure oxygen does not react with silver at room temperature. Silver oxide may be formed, however, by heating silver to high temperatures in the presence or oxygen (Davies, 1967; and Sneed, Maynard and Brasted, 1954).

Oxidation by Atomic Oxygen (O)

It has been found that silver acts as an excellent catalyst for the recombination of atomic oxygen (Kaufman, 1961) to give molecular oxygen, O_2. Since O_2 does not oxidize silver, the recombination is a competing reaction with oxidation. The recombination is quite exothermic at -117.98 kcal/mole (Kaufman, 1967). Recombination may occur in three basic ways (Wise and Wood, 1967):

(a) Two atoms adsorbed on the surface recombine and leave as a molecule (Hinshelwood mechanism).

(b) A gaseous atom combines with an atom adsorbed on the surface and the molecule is desorbed (Rideal mechanism).

(c) Two gaseous atoms combine, then hit the surface releasing the excess energy.

Thomas (1970) proposed that the Rideal mechanism is responsible for the recombination of O on silver. His conclusions are based upon both O recombination and the Rideal mechanism being first order, the Hinshelwood mechanism being second order (thus eliminating it as a possiblity) and considering (a) to be negligible. May and Linnett (1967) have found the recombination efficiency to be about 0.2.

As the silver surface becomes oxidized, Ag_2O may also participate in O recombination. A two-step mechanism has been proposed by Meyerson (1967):

$$(Ag_2O) + O \longrightarrow 2(AgO)_s \qquad (1)$$

$$(2AgO)_s + O \longrightarrow (Ag_2O)_s + O_2 \qquad (2)$$

s = surface layer

It is believed that the high efficiency for thin oxide layers may be related to the ease with which electrons may be transmitted from the metal through the oxide layer to the chemisorbed oxygen (Hardy and Linnett, 1967).

The oxidation of silver by O may be described in the following way:

$$2Ag + O \longrightarrow Ag_2O \qquad (3)$$

$$Ag + O \longrightarrow AgO \qquad (4)$$

The formation of the oxide appears to be a simple reaction but as it proceeds the reaction products form a compact phase which spacially separates the reacting substances (Ag and O) from each other (Thomas, 1970). Hence, the course of reactions is no longer described by reactions 3 and 4, but by diffusion processes and phase-boundary reactions which are very complex. Under such circumstances Hauffe (1965) indicates the following processes should be considered:

1. Phase boundary reactions, nucleation and crystal growth
2. Diffusion or transport of ions, electrons and holes through the oxide layer
3. Transport in space-charge boundary layer

4. Thermodynamic stability of the oxide that is formed

5. Crystal structure of metal and oxide layer

As with the other reactions, the slowest of these processes determines the oxidation rate If the oxide layer is porous, or if diffusion and other transport mechanisms are faster than surface reactions, then a linear rate in the growth of oxide thickness should be observed. If diffusion or transport is the controlling factor, then the parabolic or cubic rate is observed. A contact potential may be generated by the gas- oxide or oxide-metal interface which produces a field which in turn controls the transport of ions, holes, and electrons. When this is the controlling step, the logrithmic and reciprocal rates are observed. These rate laws proposed by Hauffe have been substantiated theoretically by Fromhold and Cook (1967a and 1967b).

Several chemical models have been proposed for the oxidation of silver films by atomic oxygen. Perhaps the most detailed one is proposed by Thomas and Baker (1971) and is developed in equations 5 to 12, inclusive. They use as a basis the two competing reactions proposed by Meyerson (1967).

$$O + Ag_2O \xrightarrow{k_1} (Ag\ O)_2 \qquad (5)$$

$$O + (Ag\ O)_2 \xrightarrow{k_2} Ag_2\ O + O_2 \qquad (6)$$

Equation 5 accounts for oxidation of, and 6 for recombination on,a partially oxidized silver surface. Further, they propose that silver below the film surface is oxidized by an oxygen transfer reaction (7) with $(AgO)_2$ acting as an intermediate:

$$2\ Ag + (Ag\ O)_{2s} \xrightarrow{k_3} (Ag_2O)_i + (Ag_2O)_2 \qquad (7)$$

when i indicates "interior" and s "indicates" surface. The rate of oxidation of the film from equation (7) is:

$$R = \frac{d[(AgO_2)_i]}{dt} = k_3 [(Ag)_i]^2 \; [(AgO)_{2s}] \qquad (8)$$

Using the steady state approximation for $(AgO)_2$ and considering the densities only at the surface, equations (9) and (10) result.

$$\frac{Ag_2O}{(AgO)_2} = \frac{1}{k_1}\left(k_2 + \frac{k_3[Ag]^2}{[O]}\right) \qquad (9)$$

$$[(AgO)_2] + [Ag_2O] = C \qquad (10)$$

combining equations (9) and (10) and eliminating Ag_2O the rate becomes

$$R = \frac{C\, k_1\, k_3\, [Ag]^2\, [O]}{k_1[O] + k_2[O] + k_3[Ag]^2} \qquad (11)$$

They conclude that if $[O] \ll k_3 \; [Ag]^2 / (k_1 + k_2)$ as is the case at early times in the oxidation, then the rate is proportional to the atomic oxygen flux O .

$$R = Ck_1 \, [O] \qquad (12)$$

The Thomas-Baker model by use of equation (7) predicts that silver should continue to be oxidized even after the atomic oxygen flux has stopped (referred to as coasting) if k_3 is relatively small causing O transport to become the rate controlling step. Also, this coasting should become more pronounced as the oxide layer layer builds up, decreasing the magnitude of k_3.

<u>Difficulties of the Thomas-Baker Model</u>

The Thomas-Baker model presumes the following which may introduce significant errors into the model:

1. The model does not account for the initial oxidation of the silver surface but assumes it to be oxidized to Ag_2O (see reaction 5) before reactions (5), (6), and (7) proceed. If this assumption is not valid, then the initial Ag + O reaction must be considered as competing with reactions (5) and (6).
2. The model assumes $[Ag_2O] + [(AgO)_2]$ to be a constant, C. As the underlying silver becomes oxidized via reaction (7), the region active in O transport increases in depth and C must become larger.
3. The model also assumes a film which is fairly compact such that the underlying silver is oxidizable only by transport of oxygen from the surface layer. If the film is porous and/or the oxides, then underlying silver may be oxidized without requiring the formation of an intermediate compound (e.g., $(AgO)_2$). If this is the case, then the oxidation rate law would be linear at least initially as is observed, but little coasting would be detected as observed by Henderson (1973). It would be well to mention here that coasting could also be due to extensive adsorption of atomic oxygen. The mechanism of coasting could be tested by observing the mass change of a film sufficiently thick that a substantial amount of silver was not in direct contact with the oxidizing atmosphere. Under these conditions only transport of O should be responsible for extensive oxidation as in reation (7).

Oxidation by Ozone

It has been found that ozone reacts with silver in the presence of moisture, producing AgO (Sneed, Maynard and Brasted, 1954). Galla (1961) reported oxidation of thin silver films in dilute ozone atmospheres. Henderson and Schiff (1970) have also reported that ozone reacts with thin silver film detectors but the relative efficiency is about one-hundred thousand times less than atomic oxygen. Galla, Hoeckelman and Matle (1961) found that extensive exposure of 70 Å thick silver films to ozone caused their conductivity to decrease by a factor of 0.3. After the flow of ozone was discontinued their conductivity returned to near its initial value. They conclude, based on this behavior, that no silver compounds were formed. McMillan (1962) presumes that ozone should oxidize Ag_2O to AgO. Since small quantities of Ag_2O might remain on a cycled detector, this may account for their greater sensitivity toward ozone. Silver films have also been shown to be efficient catalysts for the decomposition of ozone (Kashtanov, 1963).

Once an O_3 molecule is adsorbed on the silver surface it may undergo any one of a number of reactions. The mechanisms are not known, but some possibilities include:

1. Dissociation and recombination analogous to Meyerson (1967) on a partially oxidized surface:

   (a) $Ag_2O + O_3 \longrightarrow O_2 + (AgO)_2$

   (b) $(AgO)_2 + O_3 \longrightarrow Ag_2O + 2O_2$

2. Combining with another adsorbed O_3 on the surface:

   $$2O_3 \xrightarrow[s]{} 3O_2$$

3. Dissociation followed by further reaction of the O and desorption of the O_2 :

   (a) $O_3 \xrightarrow[s]{} O + O_2$

   (b) $O + O \longrightarrow O_2$

   (c) $2Ag + O \longrightarrow Ag_2O$

(d) $Ag_2O + O \longrightarrow (AgO)_2$

4. Formation of silver ozonide:

(a) $Ag + O_3 \longrightarrow AgO_3$

(b) $AgO_3 \longrightarrow AgO + O_2$

Mechanisms 1 and 2 could account for the catalytic behavior of silver in the decomposition of O_3. Mechanisms 3 and 4 could describe the oxidation of silver by O_3.

Generation and Measurement of Atomic Oxygen in the Laboratory

Known concentrations of atomic oxygen can be produced in the laboratory by making use of the following reaction:

$$N + NO \longrightarrow N_2 + O \tag{13}$$

This reaction is relatively fast and is experimentally stochiometric (Morgan, 1960). That is, one oxygen atom is produced for every NO molecule consumed. Thus, if the rate of disappearance of NO is known, the production rate of O is also known (i.e., they are the same). This procedure for producing atomic oxygen is commonly used and has been checked against an ESR technique by Westberg and de Haas (1964). Their results showed the two techniques agreed within experimental errors.

In the apparatus described below the NO is discharged from a known fixed volume. The delivery rate of NO can then be determined knowing the rate of pressure change.

$$\frac{dn}{dt} = \frac{dP}{dt} \frac{V}{RT} \tag{14}$$

where

$\frac{dn}{dt}$ = the molar discharge rate of NO (thus the molar production rate of O)

$\frac{dp}{dt}$ = the rate of pressure change of the NO storage and delivery system

V = volume of the NO storage and delivery system

R = gas constant

T = absolute temperature

Since both the total gas and atomic oxygen flows and pressure of the reaction cell are known, it is possible to compute the partial pressure of atomic oxygen in the reaction cell:

$$P_o = \frac{Q_o}{Q_T} P_c \qquad (15)$$

where

P_o = the partial pressure of atomic oxygen

Q_o = flow rate of atomic oxygen

Q_T = total flow rate of all the gases

P_c = pressure of the reaction cell

The reaction cell was designed to act as a stirred flow reactor with a residence time of several seconds. This met the reiterion that residence time must be long enough to break up flow patterns but not so long as to allow for appreciable recombination of atomic oxygen. The pressure of the reaction cell could also be adjusted with an auxillary vacuum pump so as to maintain the mean free particle distance longer than the dimension of the detector surface. Under these conditions there should be no significant concentration gradients develop and the collision frequency given by equation (16) should be very close to the number of particles which actually do collide with the surface per unit time.

$$Z = \frac{P_o L}{4RT} \left[\frac{8\ RT}{\pi M}\right]^{\frac{1}{2}} \qquad (16)$$

where

Z = the collision frequency

P_o = partial pressure of atomic oxygen

L = Avagadro's number

R = universal gas constant

M = molecular weight of the particle of interest

T = absolute temperature

Atomic nitrogen needed for reaction (13) can be generated from a microwave discharge (approximately 10 W at 2.45 GHZ):

$$N_2 + e^- \longrightarrow N_2^+ + 2e^- \longrightarrow N + N + e^- \qquad (17)$$

Certainly reaction (17) is not the only reaction which occurs in the discharge, but it is largely responsible for the generation of N atoms.

Atomic nitrogen thus produced can recombine in at least two ways:

$$N + N \longrightarrow N_2^* \longrightarrow N_2\ h\nu\ \text{(yellow)} \qquad (18)$$

$$N + N + M \longrightarrow N_2 + M \qquad (19)$$

Reaction (22) is responsible for the yellow afterglow observed downstream from the discharge.

With excess NO in the N + NO reaction, additional reactions occur:

$$NO + O \longrightarrow NO_2^* \longrightarrow NO_2 + h\nu\ \text{(yellow-green)} \qquad (20)$$

The system was designed such that the light output of this reaction controlled the rate at which NO flowed into the N + NO reaction. Reaction (20) was used rather than (13) or (21) because reaction (17) emits no light and the excess N of reaction (25) reduces the silver oxides while excess NO of (24) has no effect (Henderson, 1970). The NO added in this manner exceeded the stoichiometric amount by only a few percent.

With excess N atoms in the N + NO reaction, a bluish light is emitted:

$$N + O + M \longrightarrow NO^* + M$$

$$NO^* \longrightarrow NO + h\nu\ \text{(blue)}$$

Atomic oxygen produced by reaction (17) may also recombine to form molecular oxygen in the following way:

$$O + O \longrightarrow O_2^* + hv \qquad (22)$$

$$O + O + M \longrightarrow O_2 + M \qquad (23)$$

Since the calculation of atomic oxygen depends upon the concentration of atomic oxygen remaining constant, it is necessary to know to what extent reactions (26) and (27) proceed. Thomas (1970) asserts that these reactions are responsible for negligibly small loss of atomic oxygen in all-glass systems such as the one described herein. Thus, the atomic oxygen concentration should be practically constant. However, to minimize such losses the distance from the N + NO reaction to the reaction cell was made as small as possible and still provide enough time for the O generating reaction to go to completion.

When it was desirable to "turn off" the Ag + O reaction, it was done by quenching. That is, third bodies (M) were supplied to reaction (23) so recombination became very rapid. The system was designed so the silver film was located over the incoming air (source of third bodies) which brought the reaction cell very rapidly to atmospheric pressure (in under 300 milliseconds). Under these conditions the Ag + O reaction should turn off in less than one-half second.

Generation and Measurement of Ozone in the Laboratory

It was found that relatively high concentrations of ozone were required. This need was met by using ozone which was dissolved in freon kept at low temperature and high pressure. In this manner ozone concentrations from 0.05 to 3 mole percent could be supplied to the system.

The ozone concentration was measured by using Beer's law.

$$C = -\log \frac{I}{I_o} \frac{1}{\epsilon X} \tag{24}$$

where

C = concentration

I_o = light intensity

I = lifht intensity through the medium

ϵ = extinction coefficient

X = optical path length through the cell

The ozone concentration data were taken at a wavelength of 2537 Å (brightest mercury line). The extinction coefficient for ozone at this wavelength is

$$\epsilon = 134 \text{ cm}^{-1} \text{ atm}^{-1} \quad \text{(Inn and Tanaka, 1956)}$$

It was presumed (and verified by experiment) that ozone is relatively unreactive toward silver, thus no concentration gradients should develop even though the mean free path was several times shorter than the detector length. For this reason it was felt that equation (16) should hold true for ozone also.

Measurement of the Extent of Reaction Gravimetrically

The determination of small mass changes can be made by use of a quartz crystal oscillator. As mass builds up on the face of an AT cut quartz crystal, the period of harmonic oscillation lengthens. The mass change is related to the period change by the following equation (for the Kronos QM-1 Digital Thickness Monitor).

$$dM = dX \frac{NPA}{\nu S} \tag{25}$$

where:

dM = mass change

dX = change in instrument period count

N = 1670 KHZ - MM

P = density of quartz

A = crystal area

ν = reference frequency

S = scale factor (of counter electronics)

For an active crystal area of 0.713 cm^2 the sensitivity of the device used in the experiments was 1.9×10^{-8} g/count. This is equivalent to approximately 0.8 molayers of silver. The device was quite stable and a change of more than two counts was taken as significant.

Measurement of the Extent of Reaction Electircally

A very common method of determining the extent of reaction of silver film detectors is to measure their electrical resistance. Because silver is a good conductor and its oxides are not, the electrical resistance increases as the oxidation of the silver proceeds. The dynamic range of resistance encountered in this study was quite large--from about 10 Ω to more than 10^6 Ω For this reason a logrithmic ohmmeter was used to measure the resistance.

EXPERIMENTAL APPARATUS AND METHODS

Ozone and Atomic Oxygen Flow Systems

As indicated earlier, the atomic oxygen flow system was designed to minimize atomic oxygen recombination and to provide appropriate residence time and mean free path in the reaction cell minimizing concentration gradients.

Functional Description of Atomic Oxygen Apparatus

A pressure transducer in combination with the flowmeter provides a means of measuring the flow rate of nitrogen into the system. Automatic pressure controller 1 (APC1), a servovalve and pressure transducer, maintain a constant pressure in the flow manifold. The microwave source and cavity discharges the nitrogen in the flow stream to produce atomic nitrogen used in the O-producing reaction. When nitric oxide is added to reaction (13) in slight excess of the stoichiometric amount, visible light is emitted from excited NO_2. The brightness of this light is used to control the rate at which NO is added to the atomic oxygen-producing reaction. This control action is provided by the photomultiplier, and picoammeters which supply the electrical signal necessary for APC2 to operate the servovalve, which in turn allows nitric oxide to flow from a known fixed volume to the flow stream via the gas titration port. The pressure of the fixed volume is measured with a pressure transducer and indicator and recorded on the strip chart recorder. The mass added to the silver film is measured by a commercially available digital thickness monitor (DTM). In order to be recorded simultaneously with the other data the signal from the DTM was converted from digital to analog. The resistance of the silver films was measured using a log ohmmeter which had an analog signal output proportional to the logarithm of the film resistance.

Functional Description of Ozone Apparatus

The flow rate of the ozone-freon gas was determined with the flowmeter, and the flow manifold was kept at a constant pressure using APC1 in combination with a servo valve and pressure transducer. The spectrophotometer consisted of the mercury lamp, UV monochrometer, absorption cell, photomultiplier and picoammeter. The log ohmmeter and DTM served the same purpose as in the atomic oxygen flow system.

Experimental Method for Atomic Oxygen

The following procedure was used in taking data for an atomic oxygen experiment.

(1) The N_2 flow was set so that a constant pressure of 1.5 torr was maintained in the flow manifold. This corresponds to a flow of about 300 std. cc/min.

(2) The microwave discharge was initiated and adjusted to a forward power of 5 to 10 watts.

(3) The NO delivery rate was adjusted manually to a light output which corresponded to a few percent NO excess and APC2 was set to control automatically at this point.

(4) The exit port solenoid valve was opened. This corresponded to time zero, and was marked automatically on the analog record.

(5) A continuous analog record was made of the NO pressure and either the DTM or logrithmic ohmmeter output. When it was desirable to record both the DTM and logrithmic ohmmeter outputs simultaneously the NO pressure was recorded for a one minute period before admitting atomic oxygen to the reaction cell.

(6) Microwave forward power, room temperature, flowmeter reading, and reaction cell pressure were noted.

Experimental Method for Ozone

The following procedure was used in taking data for an ozone experiment.

(1) the ozone-freon flow rate was adjusted with APC1 so that a constant pressure of 70 torr was maintained in the flow manifold.

(2) The bypass valve was opened to permit all the flow to pass into the reaction cell. This corresponded to time zero.

(3) The room temperature, flowmeter reading, and reaction cell pressure were noted.

(4) The ozone concentration was measured with the spectrophotometer system by noting the light intensity with and without the ozone-freon flow established prior to time zero.

(5) An analog record was made of the DTM output and/or the resistance change of a silver film detector.

Experimental Method for Reduction of AgO_x

Two different methods were used to reduce silver films which were previously oxidized--flame reduction and active nitrogen reduction. Flame reduction was accomplished by passing the film several times through an oxygen-methan flame several millimeters above the most luminous cone. Active nitrogen reduction consisted of exposing the film to nitrogen discharged in a microwave cavity at 1 or 2 torr and 20 to 40 watts.

RESULTS AND DISCUSSION

In the course of this study, which was primarily designed to determine the relative rates of reaction of atomic oxygen and ozone with silver surfaces, a number of phenomena have been observed. While they have not yet received exhaustive study, they deserve comment in this paper.

A phenomenon of some interest is the reduction of silver films which have previously been oxidized by atomic oxygen. Thomas (1970) reported the reduction of silver films by active nitrogen and Henderson (1970) by active hydrogen. In his work, Thomas (1970) established that the nature of the silver film is changed substantially after having been oxidized and reduced. The silver becomes a matted grey color and the film, when used as a detector, becomes more sensitive to atomic oxygen. We have found additionally that reduction is very rapid when the oxidized film is passed quickly through a methan-oxygen flame. The current hypothesis is that this is due to OH and possibly HO_2 of H_2O_2 present in the flame. Reduction could also be a result of the heat as both AgO and Ag_2O decompose above 200° C. No quantitative work on this process has yet been performed.

A further phenomenon which has been observed is "resistance coasting"; that is to say, the electrical resistance of the film continues to increase for a short time even after the reaction with atomic oxygen has ceased. Thomas (1971) has discussed this process in some detail. Henderson (1973), however, indicated that he has not observed any significant overshoot in his experiments. Thomas and Baker (1971) presume that coasting may be due to the formation of AgO on the surface followed by the migration of oxygen to the interior of the film to form Ag_2O. If this hypothesis is correct, then there should be a limit to the rate at which atomic oxygen can be delivered to the surface without causing nonlinear effects. To study these effects we have performed an experiment in a different fashion than either Thomas or Henderson. In it the silver-atomic oxygen reaction is turned off by admitting suddenly (within 50 ms) an atmosphere of gas. This effectively eliminates all the atomic oxygen via three-body processes. Figure 3 shows the results of one of these experiments, which does, indeed, indicate the existence of coasting in the resistance curve. It was also found that this effect was more pronounced when the resistance had increased more than two orders of magnitude from its initial value. This may in part explain the differences between the observations of Thomas and Henderson.

It is common in a chemical kinetic study to express the experimental results in terms of a rate law which relates a measured parameter of the reaction to the time integrated or differential concentrations of the chemical species involved. Time integral concentrations (e.g., total number of particles to the surface of the film) and resistance are often used in studies of thin silver films used as atomic oxygen detectors. This has the disadvatnage that the change in resistance may be quantitatively very complex when related to other reaction parameters. In this study, therefore, we have chosen to use the mass accumulated by the film as a function of the exposure of the film to a given number of particles of atomoc oxygen or ozone.

In our work we find that the behavior of the reaction process does not follow a simple rate law, although over the rane in which there is relatively little exposure to the reaction species, the data fit a linear rate law to a reasonable approximation. This result is shown in Figures 4 and 5. If these data are interpreted in terms of sticking coefficients, the initial coefficient

Figure 3

ATOMIC OXYGEN APPARATUS

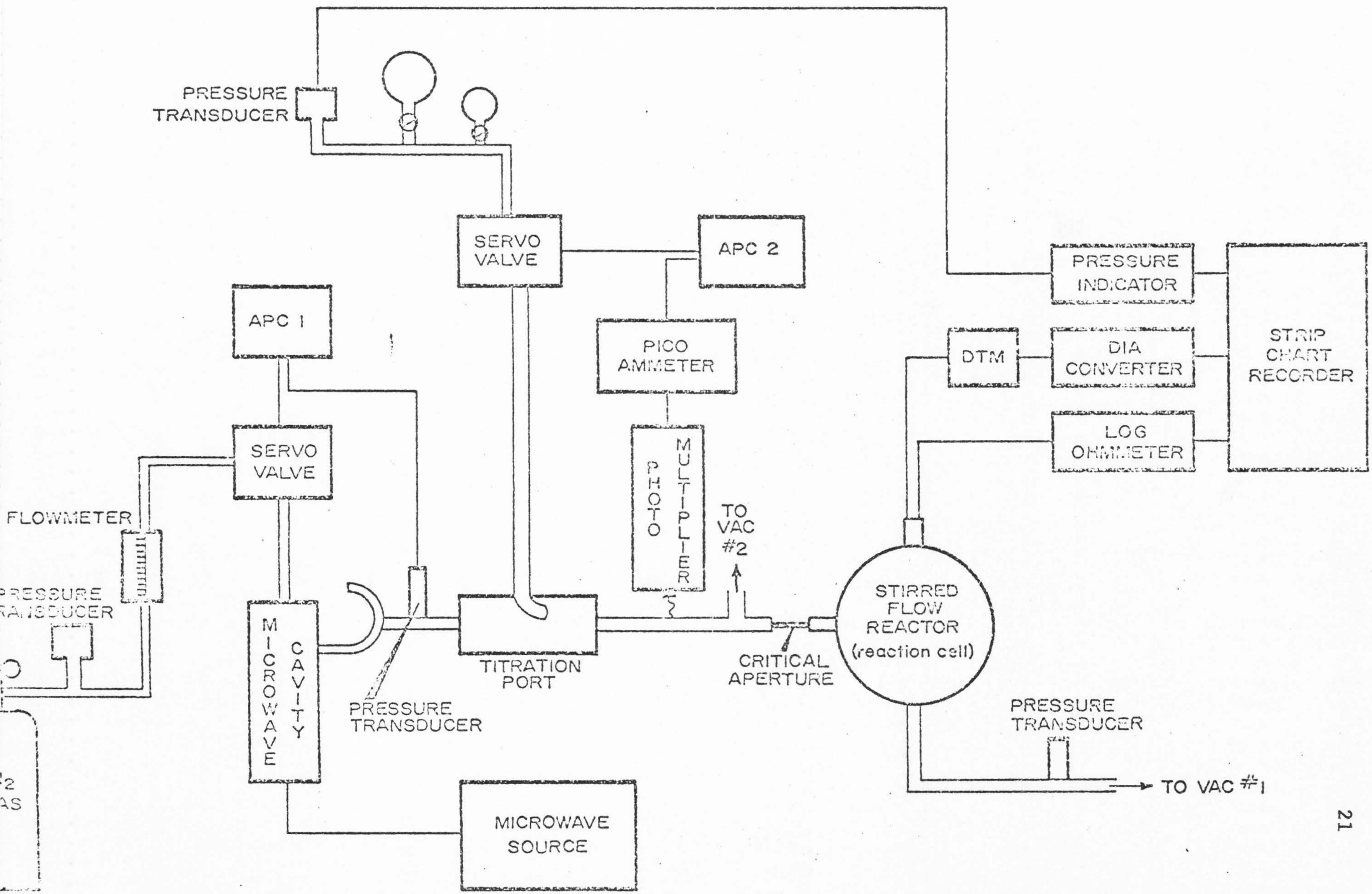


Figure 4

OZONE APPARATUS

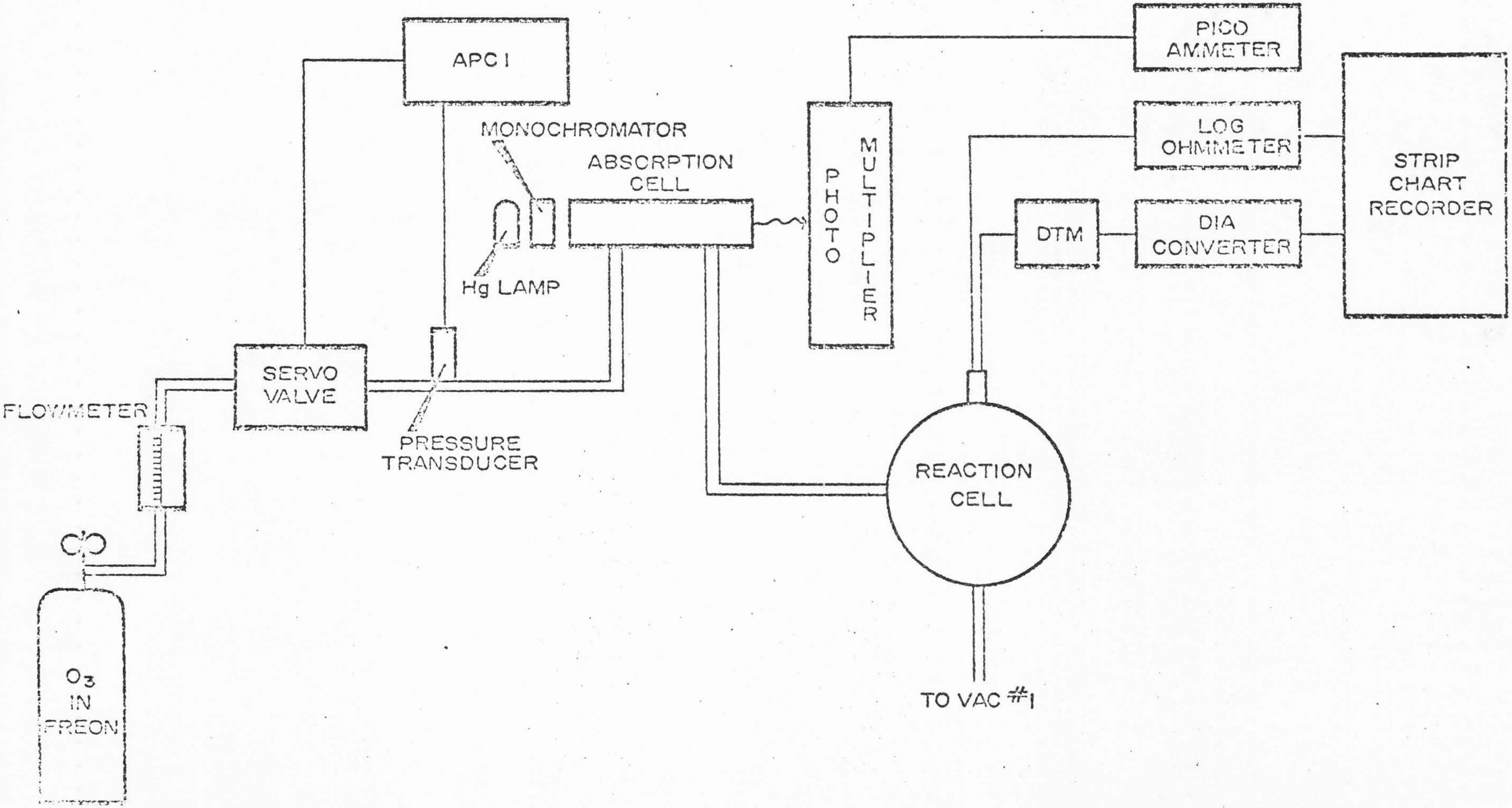
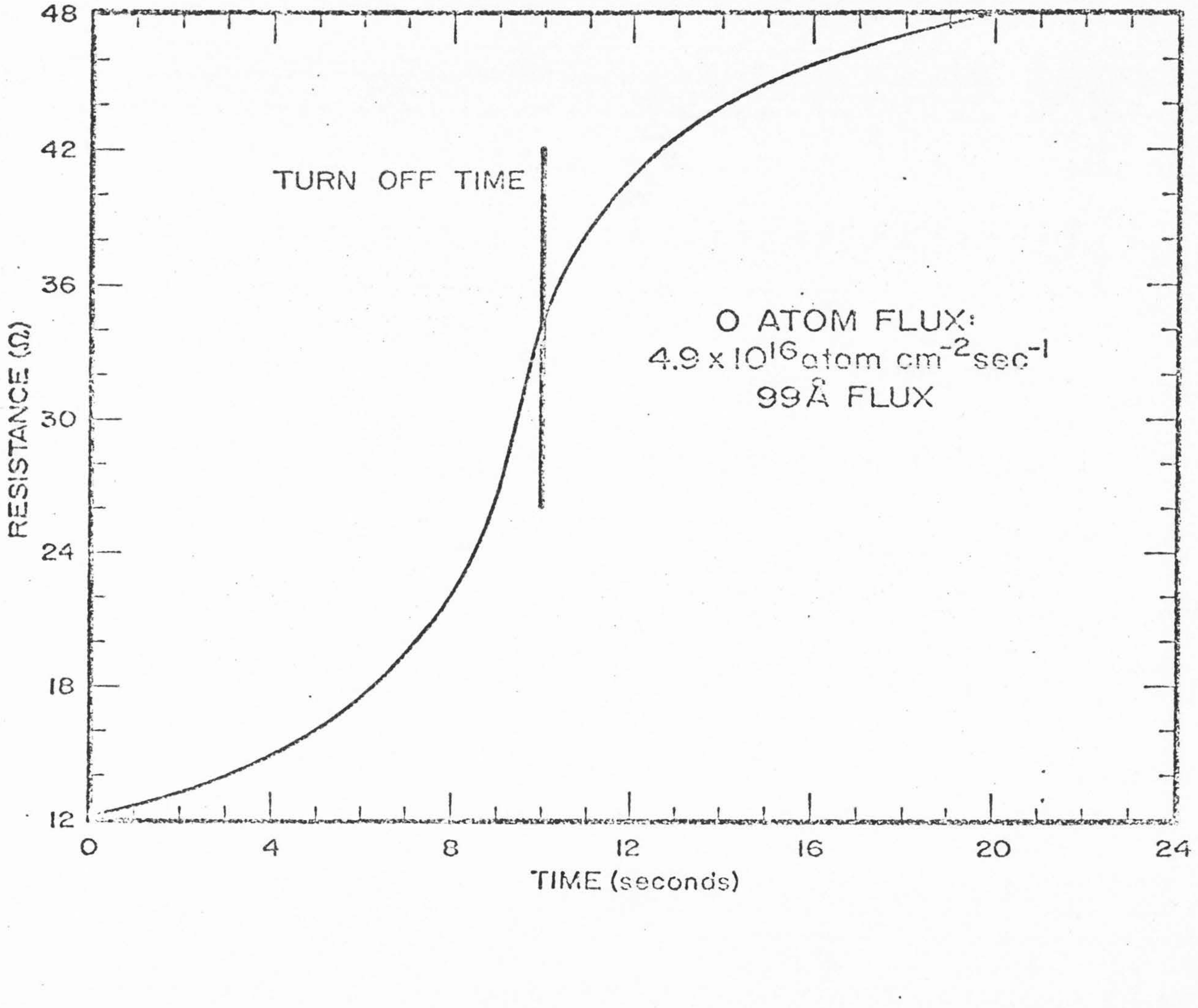


Figure 5

RESISTANCE COASTING EFFECT



for the atomic oxygen reaction is 2.8×10^{-2} and $t.0 \times 10^{-5}$ for the ozone reaction.

Coasting and initial linear rate law are both supportive evidences for the Thomas-Baker chemical model. However, if the oxides and the film are extremely porous, then coasting could result from extensively adsorbed atomic oxygen. This would also produce a linear rate law as the Ag + O reaction would predominate. These effects could be tested by measuring the coasting effects of a film which was thick and dense, thus restricting extensive oxidation to go via the Thomas-Baker model.

One of the motivations for studying the response of thin silver films to active species stems from the fact that such films are nearly specific to atomic oxygen. They therefore can be used to measure atomic oxygen height profiles in the region below 100 km in which the use of mass spectrometers has been extremely difficult. The species which is most likely to compete with atomic oxygen in the reaction with silver films in this region is ozone. In this study it was found that exposure to ozone caused a cycled detector (i.e., one which had been oxidized then reduced) to gain mass at a rate 6×10^{-4} as fast as a similar one exposed to atomic oxygen. If the resistance change vs. mass added is the same for the ozone and atomic oxygen reactions, then atomic oxygen detectors should be usable down to altitudes at which $[O]/[O_3]$ is approximately 6×10^{-4}. Reference to Figure 6 shows that this is reached at about 38 km for daytime conditions. At night, however, the atomic oxygen recombines and the $[O]/[O_3]$ ratio approaches zero below 70 km. This suggests that silver film atomic oxygen detectors are more usable during daylight hours.

The daytime ratio of $[O]/[O_3]$ is a very important parameter in the

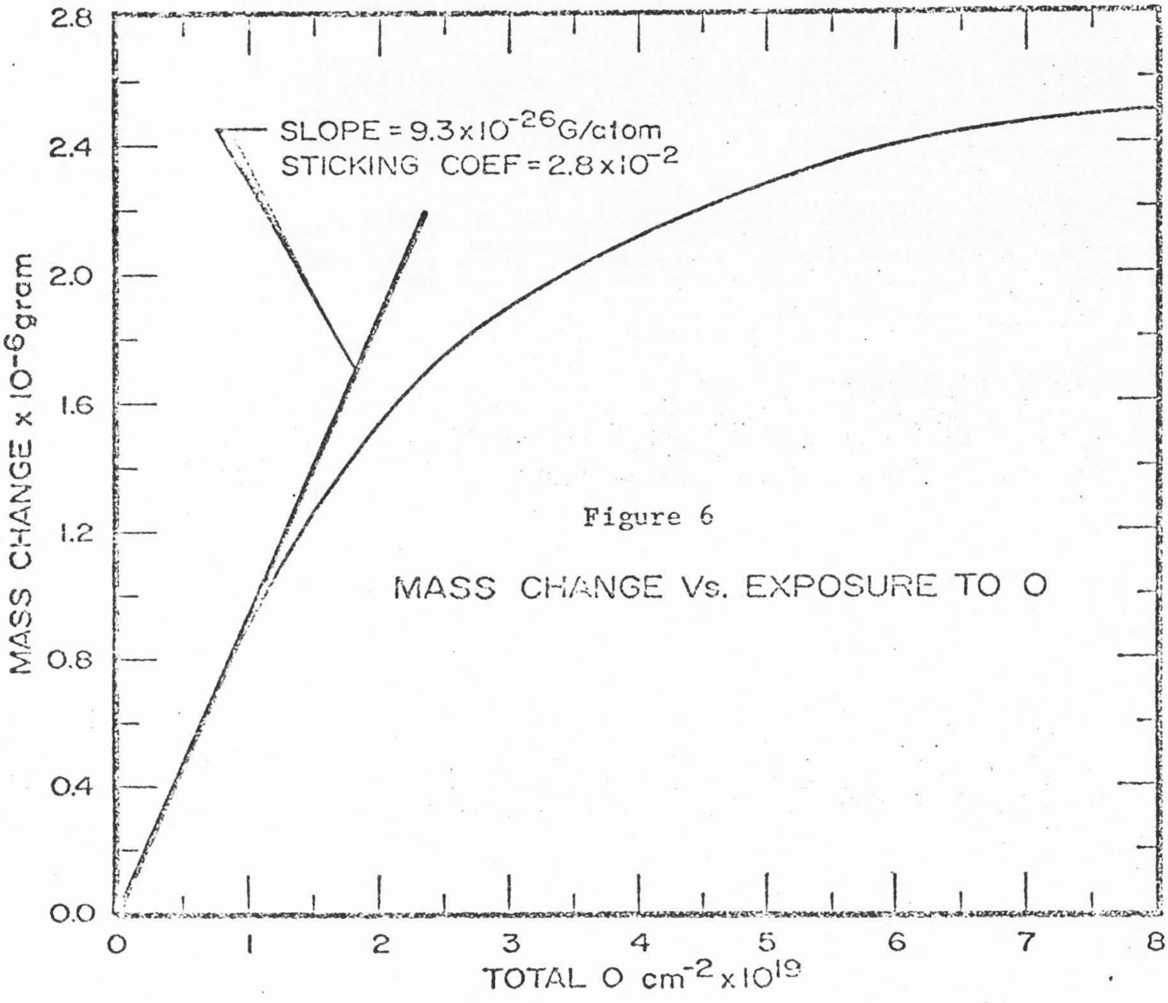


Figure 6

MASS CHANGE Vs. EXPOSURE TO O

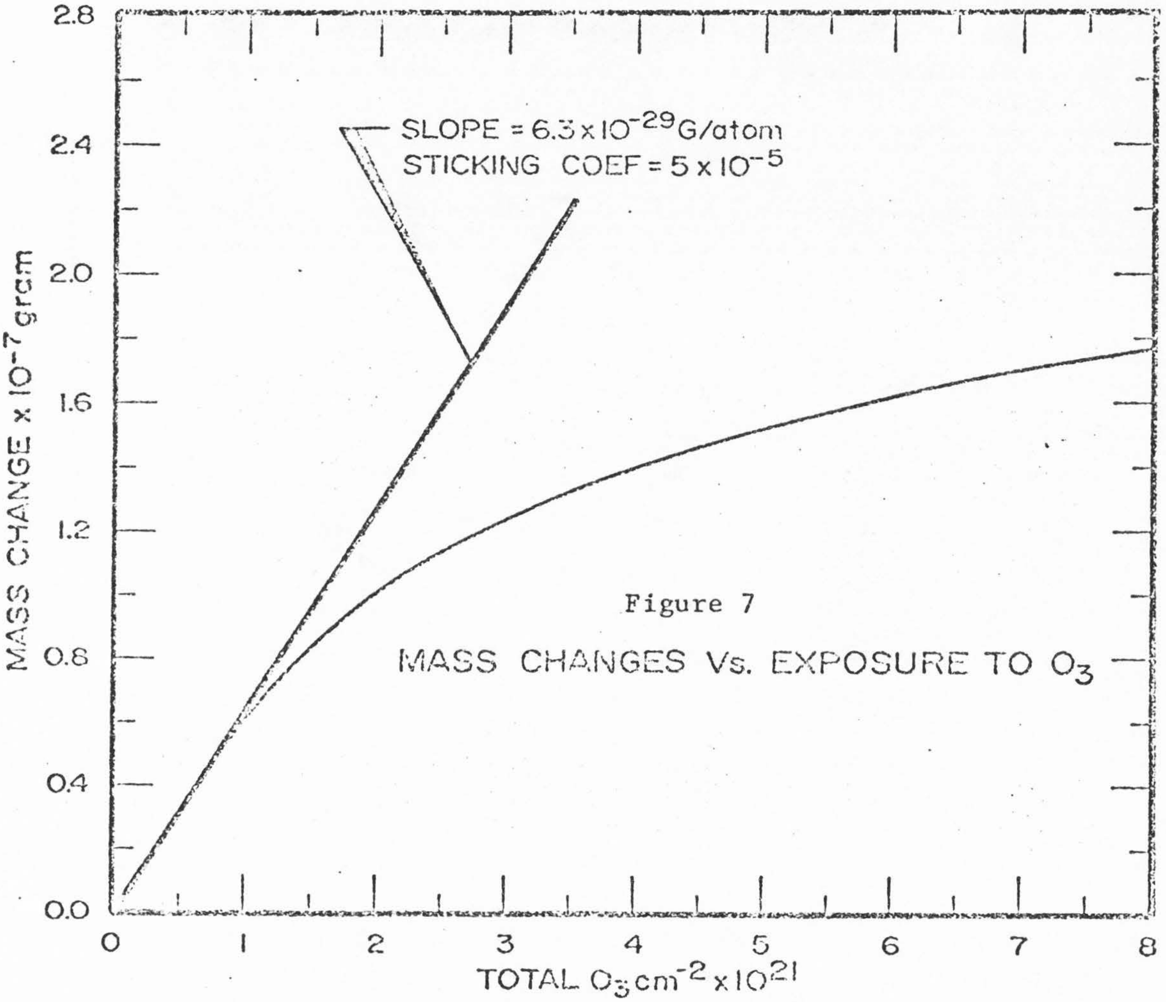


Figure 7

MASS CHANGES Vs. EXPOSURE TO O_3

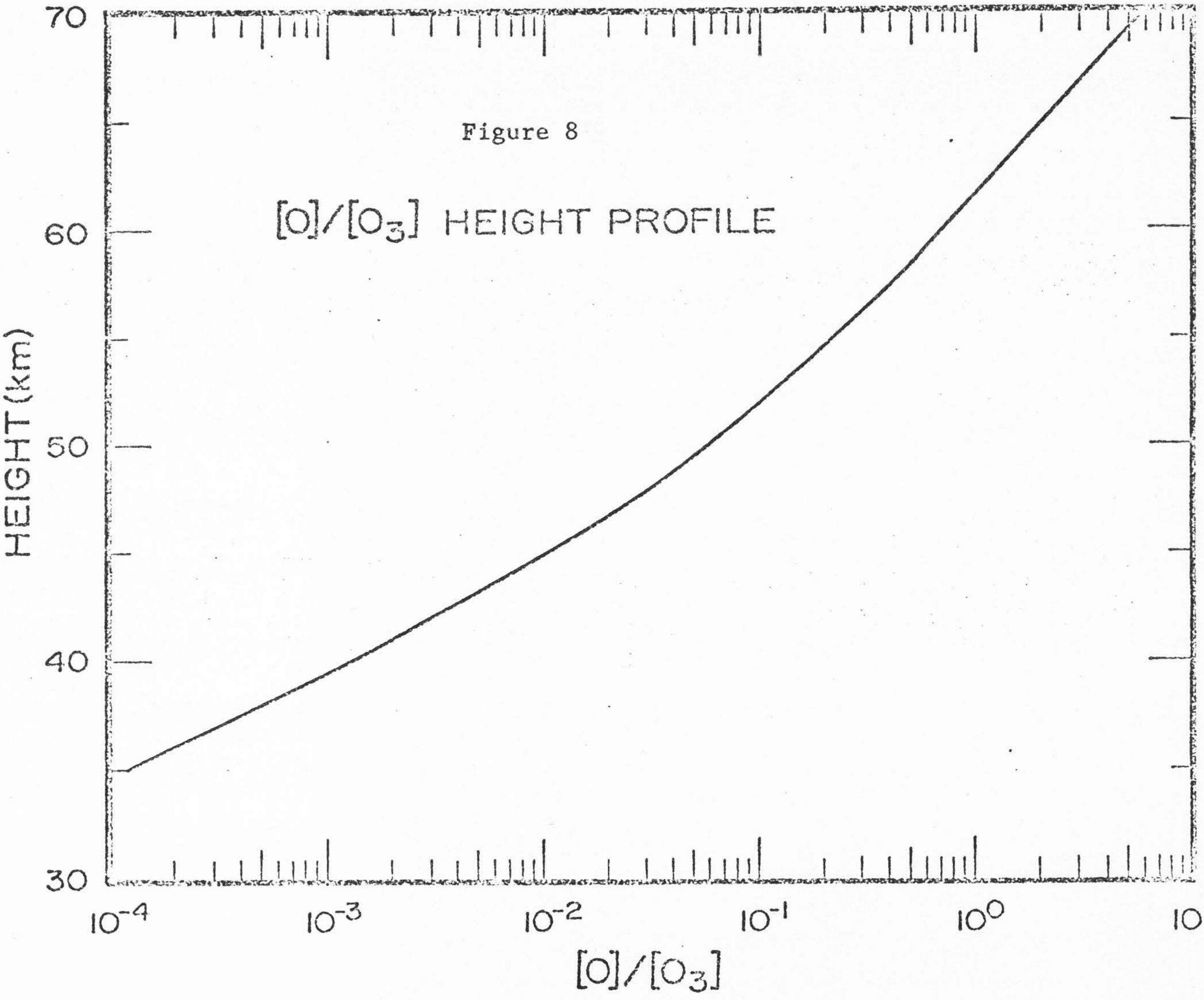


Figure 8

$[O]/[O_3]$ HEIGHT PROFILE

study of mesospheric chemistry. It appears that a silver film detector aboard a parachute-borne payload might be a viable measuring technique. At altitudes near 50 km, however, the OH radical reaches significant concentrations and its reactivity toward silver oxides may be such that substantial errors would be introduced into the measurement of atomic oxygen. Plans are being made to determine this sensitivity to OH with the idea that if sufficiently sensitive, oxidized silver films could be used as OH detectors.

CONCLUSIONS

We have investigated the nature of the reactions of thin silver films with atomic oxygen and ozone. We find that the reaction with ozone is extremely slow compared to the reaction with atomic oxygen. In terms of the application of these results to atmospheric measurements, this result indicates a useful altitude range of cycled thin silver film atomic oxygen detectors from 38 km and up. Also, the sticking coefficients of atomic oxygen and ozone on cycled thin silver films are 2.8×10^{-2} and 5×10^{-5}, respectively.

LITERATURE CITED

Bennett, H. E., R. B. Peck, D. K. Burge, and J. M. Bennett. 1969b. Formation and growth of tarnish on evaporated silver films. Journal of Applied Physics 40:3351-3360.

Bond, G. C. 1962. Catalysis by metals. Academic Press, New York. 519 p.

Czanderna, A. W. 1964. The adsorption of oxygen on silver. Journal of Physical Chemistry 68:2765.

Davies, D. E. 1957. Oxide films on silver at high termperatures. Nature 179:1293-1294.

Fromhold, A. T., Jr., and E. L. Cook. 1967a. Kinetics of oxide film growth on metal crystals: Thermal electron emission and ionic diffusion. Physical Review 163:650-664.

Fromhold, A. T., Jr., and E. L. Cook. 1967b. Kinetics of oxide film growth on metal crystals: Electron tunneling and ionic diffusion. Physical Review 158:600-612.

Galla, R. T., R. F. Hoeckelman and C. C. Matle. 1961. In 1961 Transactions of the English vacuum symposum and Second International Congress. Pergamon Press, New York.

Hardy, W. A., and J. W. Linnett. 1967. Mechanisms of atom recombination on surfaces. Eleventh Symposium on Combustion, Combustion Institute, Pittsburgh, Pennsylvania. pp. 167-176.

Hauffe, K. 1965. Oxidation of metals. Plenum Press, New York. 452 p.

Henderson, W. R., and H. I Schiff. 1970. Planet Space Sci., 1970, Vol. 18. pp. 1527-1534. Pergamon Press, New York.

Henderson, W. R. 1973. In private conversation with L. R. Megill.

Inn, E. C. Y. and Y. Tanaka. 1959. Ozone absorption coefficients in the visible and ultraviolet regions. In Ozone Chemistry and Technology. American Chemical Society, Washington, D. C.

Kashtanov, L. I., N. P. Ivanova and V. P. Ryzhkov. Catalytic decomposition of ozone by various metallic surfaces. Journal of Applied Chemistry (USSR) 9, 2176-78.

Kaufman, F. 1961. Reaction of oxygen atoms. In Progress in Reaction Kinetc, G. Porter (ed.) Vol. I, pp. 1-39.

Kaufman, F. 1967. DASA reaction rate handbook. DASA Information and Analysis Center, Santa Barbara, California.

May, J. W., and J. W. Linnett. 1967. Recombination of atoms at surfaces: An effusion method applied to oxygen atom recombination. Journal of Catalysis 7:324-341.

McMillan, J. A. 1960. Magnetic properties and crystalline structure of AgO. Journal of Inorganic Nuclear Chemistry 13:28-31.

McMillan, J. A. 1962. Higher oxidation states of silver. Chemical Review 62:65-80.

Meyerson, A. L. 1963. Silver-catalyzed recombination in a step-function flow of atomic oxygen. Journal of Chemical Physics 38:2043-2045.

Morgan, J. E., L. Elias, and H. I. Schiff, Jr. 1960. Chem. Phys. 33:930.

Scatturin, V., P. H. Bellon, and A. J. Salkind. 1961. The structure of silver oxide determined by means of neutron diffraction. Electrochemical Society Journal 108:819-822.

Servian, J. L., and H. B. Buenafama. 1969. On the structure of AgO. Inorganic and Nuclear Chemistry Letters 5:337-338.

Sneed, M. C., J. L. Maynard, and R. C. Brasted. 1954. Comprehensive inorganic chemistry. Vol. II of Copper, Silver and Gold. D. Van Nostrand Company, Inc., New York. 248 p.

Thomas, R. J. 1970. A thin film silver detector for the direct measurement of atomic oxygen in the upper atmosphere. Electrodynamics Laboratories Report.

Thomas, R. J., and D. J. Baker (197?) Silver film atomic oxygen sensors. A report for the Center for Research in Aeronomy, Utah State University, Logan, Utah.

Weast, R. C. 1967. Handbook of Chemistry and Physics, 48th Edition. The Chemical Rubber Company, Cleveland, Ohio.

Westenberg, A. A., and N. de Haas. 1964. Quantitative measurements of gas phase O and N atom concentrations by ESR. Journal of Chemical Physics 40:3087-3098.

Wise, H., and B. J. Wood. 1967. Reactive collisions between gas and surface atoms. In Advances in Atomic and Molecular Physics, D. R. Bates and I. Estesmann (eds.), Vol. III. Academic Press, New York. pp. 291-354.