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Technical Status Report No. 4
A Study of the Effect of Surfaces on Oxygen Atom
Recombination at Low Pressures

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Summary

Equipment has been designed, built, and operated over the last two years simulating satellite environment for the study of the effect of surfaces interacting with O-atoms. The most pertinent metals from the standpoint of current use (silver, titanium, gold and stainless steel) have all been tested. The results show that these are not good metals for fabrication under many conditions of satellite mass spectrometric measurements. These results are basically in accord with the observed satellite measurements.

A modified system is now operable for rapid testing of additional promising materials. It is planned to obtain additional results with mixtures of oxygen and H-atoms as atomic hydrogen is also a constituent of our rarefied upper atmosphere.

Introduction

The pressure regime within which these studies are made is such that all gases present have mean free paths much greater than the laboratory apparatus. Since atomic oxygen colliding with any material may be destroyed it is not unusual to observe a total loss of any reactive species when special care is not taken. The approach used here was to extrapolate from an experimental arrangement used successfully several years earlier in the 10^{-2} torr pressure range.

A step by step modification has been made in the apparatus to arrive at an efficiently working system which can give a rapid determination of a recombination coefficient for a surface. A systematic search is underway to obtain practical materials of

construction to use under the unique conditions of space.

All the results to-date have been compatible with the literature values and/or the satellite measurements. This is very gratifying but does not yield a direct solution to the problem. Perhaps one important point should be noted; that is, a first order loss mechanism has been observed in all cases to-date indicating that under these conditions the O-atom loss is only proportional to the concentration of oxygen atoms.

Experimental

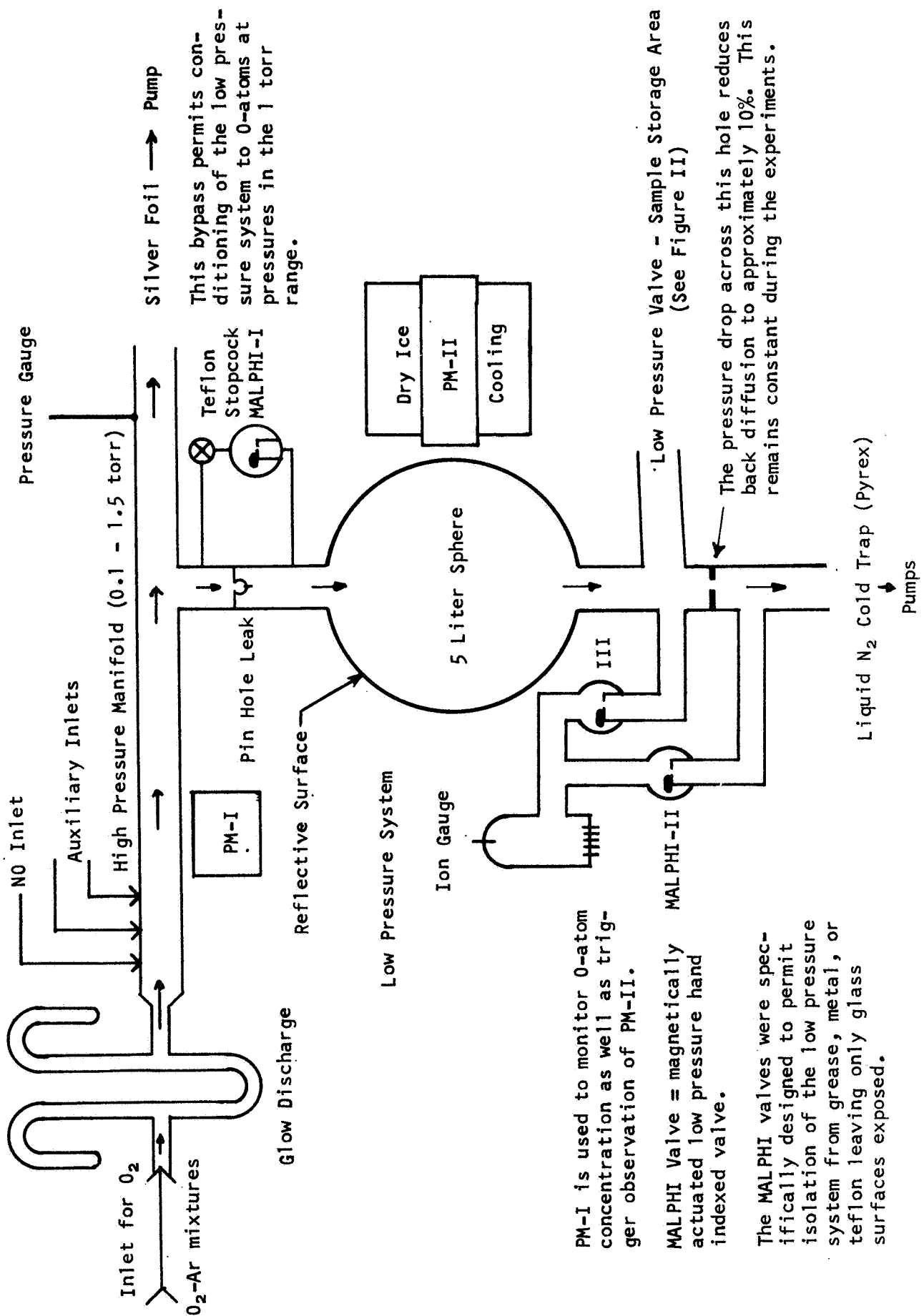
The experimental apparatus, as used and modified, has been described in previous reports. Briefly, an oxygen atom stream is generated in the 1 torr pressure region and the O-atom concentration determined by titration. A small side-stream is directed into the the very low pressure reaction system in the 10^{-5} torr or less region. First the O-atoms were shown to survive the flow system when no metal was present by freezing the radicals with liquid helium. The ozone produced quantitatively on warming could then be measured. Subsequently using a 5A adsorbent or silica gel the ozone could be frozen out with liquid nitrogen rather than helium, but the integrated measure of O-atoms via ozone formed permitted only a slow point by point accumulation of data. However, the observed formation of ozone in both cases had the very important asset of confirming without question the existence of the O-atom stream.

An evaluation of the latest equipment and techniques used for light measurement showed that the chemiluminescent technique that

we had used in the 10^{-2} torr pressure region in the past could be extended to this 10^{-5} torr range. A photomultiplier with a continuous output could within a few seconds give a reasonable O-atom recombination coefficient. At first liquid helium was used for pumping but a high capacity vacuum system with an all glass cold trap is now used. A schematic of this latest arrangement is shown in figure 1. Details are not shown for the light traps (Wood's horns). A specially designed all glass (MALPHI) valve is used extensively to avoid interaction with O-atoms (see figures 1 and 2). A sample can now be brought into the system, tested, and removed using a storage chamber which is incorporated into the reaction chamber via another large glass valve. Six or more test specimens can be stored and each tested separately under basically the same conditions with blank runs made between each without exposing the system to the atmosphere. This chamber is shown in figure 2.

Summary of Experimental Results

In the last two years studies have shown that gold, silver, stainless steel and titanium are all generally poor metals to be used as exposed surfaces in the inlet systems of satellite mass spectrometers. All these metals interact significantly with O-atoms and a complete characterization of this interaction is difficult. Insulating materials such as enamel chips were found to interact with the O-atoms as strongly as the metals tested. The most inert material to date is glass (pyrex) of which the apparatus is constructed. Typical recombination efficiencies for oxygen atoms on various surfaces at room temperature are given

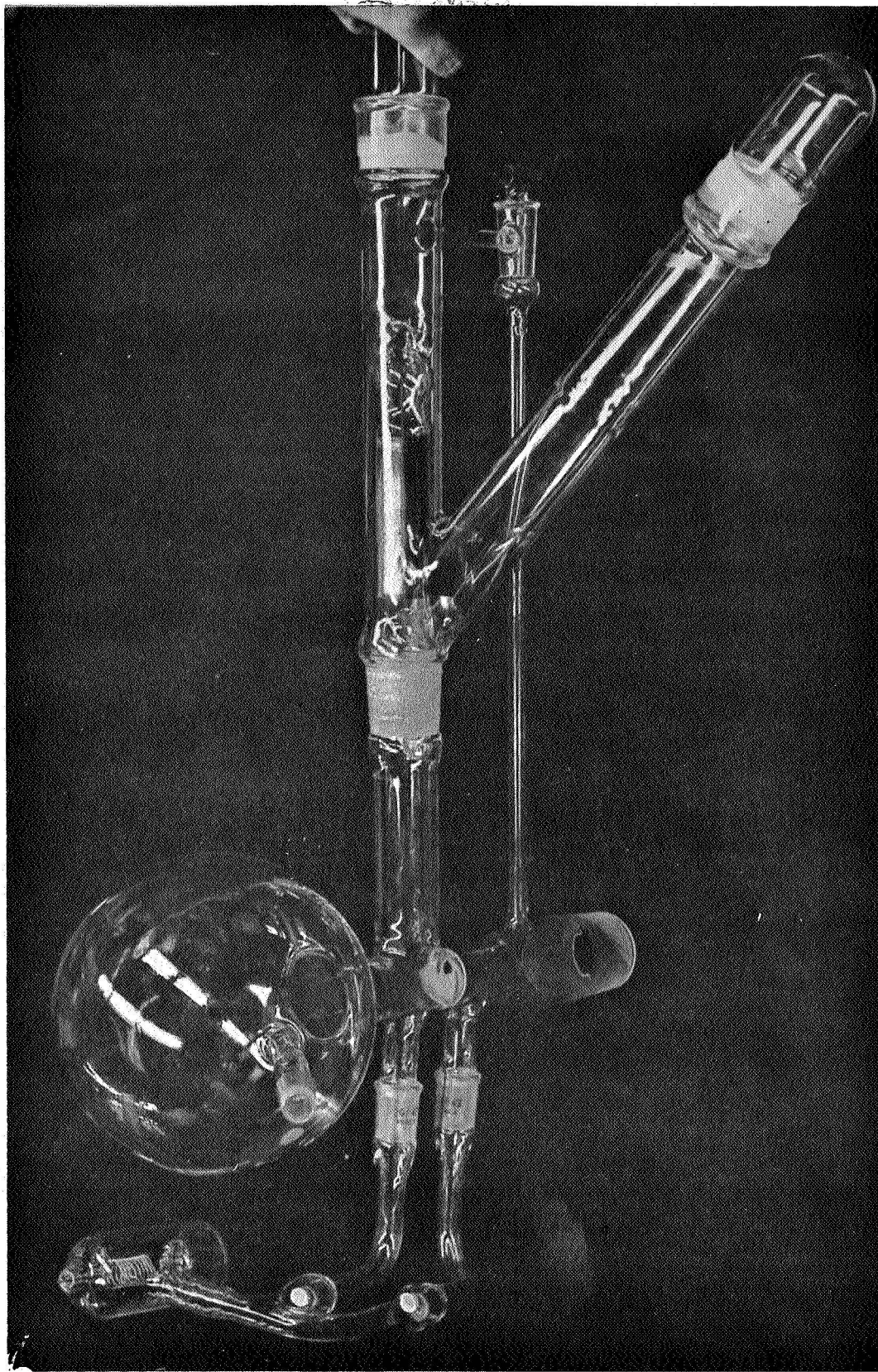


PM-I is used to monitor 0-atom concentration as well as trigger observation of PM-II.

MALPHI Valve = magnetically actuated low pressure hand indexed valve.

The MALPHI valves were specifically designed to permit isolation of the low pressure system from grease, metal, or teflon leaving only glass surfaces exposed.

Figure 1



Photograph of reaction chamber illustrating the sample storage area and valve used in isolating it from the reaction chamber.

Figure 2.

in Table I. The overall method used in this technique to obtain the data and from this calculate γ has been given previously. In the Appendix, however, is also given a description in greater detail to facilitate a more complete understanding. The results appear to be reasonable in connection with other work in the literature at considerably higher pressures.

Aluminum may prove to offer a promisingly inert surface. At the lower pressures used ($<10^{-6}$ torr) so far on a limited number of samples more rapid recombination occurred than was expected and additional study is needed to see if this is generally true or a function of the particular group of specimens, surface treatment, or other factors. A ceramic sample studied had a relatively high recombination rate for O-atoms. Several other promising specimens have been obtained for testing. One is a ceramic of especially low porosity (Mikroy 750 of Molecular Dielectrics, Inc.).

It should be emphasized that an inert surface such as a "properly prepared" aluminum may be stable and operate satisfactorily for extended periods. Other metals may also be satisfactory and basically inert. However, gold and similar metals are apparently basically reactive or interacting with the oxygen atoms especially when carefully cleaned or baked. Such reactivity is particularly detrimental when a significant number of collisions may occur before entering the ionization chamber of the mass spectrometer.

In each case the decay of the afterglow was observed to decrease exponentially with time indicating that the oxygen atoms were destroyed by a first order process proportional to the

TABLE 1
 TYPICAL RECOMBINATION EFFICIENCIES FOR OXYGEN ATOMS ON
 VARIOUS SURFACES AT ROOM TEMPERATURE

<u>Metals</u>	<u>γ</u>
Gold plate (supplied by NASA)*	0.0060
Gold sheet	0.0033
Al (commercial untreated foil)	0.0032
Al 1100 (rough surface)	0.050
Ta	0.0058
Stainless Steel	0.036
Ni	0.040
Ag**	>0.05
Ti (clean surface)***	>0.05
Ti (oxidized surface)***	<0.001
<u>Non-Metals</u>	
Glass (pyrex)	<0.0001
Enamel Chips	0.016

*The reports of Wise and Wood give several values for γ for gold considerably higher than these. Evaluation of differences in conditions did not yield a reasonable explanation although the variation in their values (0.065-0.27) may imply an inherent limitation. A recent study by Myerson (J. Chem. Phys 50, 1228 (1969)) obtained a value of 0.005 in the torr pressure range.

** The silver surface becomes oxidized and more reactive with time.

*** $Ti + O \rightarrow TiO\uparrow$ (evaporates); $TiO + O \rightarrow Ti + O_2$; and $TiO + O \rightarrow TiO_2$. TiO_2 is apparently inert, but TiO volatilizes and can cause O-atom consumption for an extended period.

O-atom concentration. This was true when NO was added as a stable reactant and the light intensity of the reaction ($\text{NO} + \text{O} \rightarrow \text{NO}_2 + h\nu$) monitored. This was also true when SO was used to generate the light by the reaction $\text{SO} + \text{O} \rightarrow \text{SO}_2 + h\nu$ where the oxygen atoms must generate the SO via the reaction $\text{COS} + \text{O} \rightarrow \text{CO} + \text{SO}$. The light intensity in this case showed a second order loss as would be expected since with no metal present the O-atoms and SO were pumped away simultaneously.

Discussion

The product of the research to-date has been the evaluation of the recombination coefficient, γ , as is given in Table 1. The obvious questions are the correctness of these values, what are γ 's for other metals, and does γ change as other parameters such as the addition of H atoms as would be present in the satellite environment. The results appear to be in line with the known experimental facts from the satellites and recombination coefficients found at low pressures might be anticipated to be less than or equal to Myerson's result of 0.005 in the 1 torr pressure range. Our results of 0.006 and 0.0033 reported prior to Myerson's publication are in amazing agreement considering the variation that may occur from one gold sample to another.

One may object in principle, however, to the use of the chemiluminescent method as extended for the O-atom concentration measurement. The enormous effort now being made at Bonn on a variety of atmospheric problems at low pressure has already yielded results strongly supporting our conclusions. Many works, however, have

contradicted this generally due to a lack of understanding of the problems of back diffusion for gas and reaction kinetics at very low pressures. A discussion concerning these problems of back diffusion is given in the Appendix.

Our approach attempts to evaluate surfaces to be used in satellite mass spectrometry utilizing our extended chemiluminescence technique. Alternatively, a mass spectrometer could be used to measure precise oxygen atom concentrations. Normally, however, this cannot be done in the laboratory because of similar problems to those found in the satellite spectrometers. To achieve accurate O-atom concentrations in this way elaborate experimental equipment is necessary including differential pumping with the reaction chamber maintained at relatively high pressures. The appearance of a variety of residual impurities such as CO, CO₂ and H₂O which are known to contribute to the background peak create additional problems for the mass spectrometrists. Since one group is already heavily committed in this direction our alternate approach seems particularly attractive. The results to date appear to justify the approach and are particularly gratifying.

A paper was presented at the ACS meeting in Minnesota entitled "Catalytic Recombination of Oxygen Atoms on Metal Surfaces in the 10⁻⁴ to 10⁻⁶ torr Pressure Range" in April. An additional paper related to the topic was presented to the International Chemiluminescence Conference at Hot Springs, California in March entitled "Chemiluminescence in the Gas Phase from Oxygen Atom

Reactions". A copy of the paper to be submitted as part of the latter conference will be forwarded in the near future. A publication is also to be submitted to the Journal of Physical Chemistry.

Appendix

Back Diffusion and Titration Errors

A major difficulty in oxygen atom studies is the loss of oxygen atoms by back diffusion. The resultant lowering of atom concentration frequently results in a misinterpretation of data. The following example is a simple case illustrating the problem.

Consider Poiseuille's equation for flow of a gas through a tube

$$\left. \frac{dV}{dt} \right|_{P_0} = \frac{\pi(P_1^2 - P_2^2) R^4}{16 L \eta P_0} \quad \text{where} \quad (1)$$

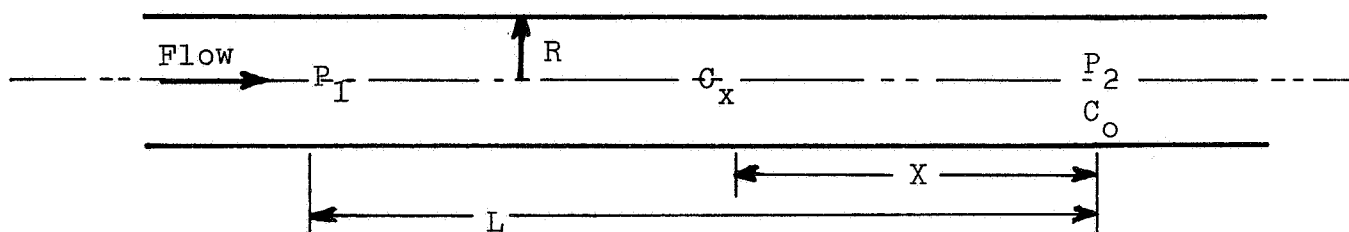


Figure 3

$\left. \frac{dV}{dt} \right|_{P_0}$ = volume flow rate in cm^3/sec measured at pressure P_0 .

P_0 = pressure at which the volume flow rate is measured in dynes/cm^2

P_1 = pressure at point (1) in dynes/cm^2 .

P_2 = pressure at point (2) in dynes/cm^2 .

L = length of the tube between points (1) and (2) in cm.

R = radius of the tube in cm.

η = viscosity of the gas in poise.

Let $P_1 = 20$ millitorr, $P_2 = 17$ millitorr, $L = 200$ cm, $R = 10$ cm, $\eta = 2 \times 10^{-4}$ poise, and $P_0 = 20$ millitorr. Then since 1 millitorr corresponds to a pressure of 1.33 dynes/cm² equation (1) becomes

$$\left. \frac{dV}{dt} \right|_{20 \text{ millitorr}} = \frac{(3.14) [(20)^2 - (17)^2] (1.33) (10)^4}{(16) (200) (2 \times 10^{-4}) (20)}$$

$$= 3.62 \times 10^5 \text{ cm}^3/\text{sec}.$$

to find the velocity of the gas stream (v) in the tube divide the volume flow rate by the cross sectional area of the tube. Thus the velocity of the gas flow is $(3.62 \times 10^5 \text{ cm}^3/\text{sec}) / (3.14)(10)^2$ or $v = 1.15 \times 10^3$ cm/sec.

If a trace concentration (C_0) is introduced at point (2) and its concentration at some point (X) upstream due to diffusion against the flow is desired one must consider Fick's law of diffusion. That is

$$\frac{dn}{dt} = -DA \frac{dC_x}{dX} \quad (2)$$

where $\frac{dn}{dt}$ = the number of particles crossing a 1 cm^2 area/sec.

D = the diffusion coefficient in $\text{cm}^2\text{-sec}$.

A = cross sectional area of tube in cm^2 .

C = the concentration in particles/ cm^3 .

X = distance upstream from the point of introduction.

$\frac{dC_x}{dX}$ = concentration gradient in particles/ cm^4 .

Thus in the case of the tube of this example

$$\frac{dn}{dt} = C_x v = -D \frac{dC_x}{dx} \quad (3)$$

Rearranging this becomes

$$-\frac{v}{D} dx = \frac{dC_x}{C_x} = d \ln C_x \quad (4)$$

Integrating the above equation from $x = 0$ to $x = x$ and $C_x = C_o$ to $C_x = C_x$ it becomes on rearrangement

$$C_x = C_o \exp(-vX/D) \quad (5)$$

This equation (5) is generally known as the Hertz equation. If we insert $v = 1.15 \times 10^3$ cm/sec and

$$D = (0.2) \frac{760}{20 \times 10^{-3}} = 7.6 \times 10^3 \text{ cm}^2 \text{ sec.}$$

into (5) it becomes

$$C_x = C_o \exp \left(-\left(\frac{1.15 \times 10^3}{7.6 \times 10^3} \right) X \right) = C_o \exp(-0.15 X)$$

or $C_x = C_o 10^{-0.0657X}$. Thus it is seen that at a distance of $X = (1/0.0657) = 15.2$ cm upstream $C_x = C_o/10$.

Likewise $C_x = C_o/100$ when $X = 30.4$ cm. This is to say that in the above example the trace impurity concentration at a distance 15.2 cm upstream from point (2) is one-tenth (10%) of that at the point of introduction, (2).

With this example as a basis consider the trace concentration to be oxygen molecules formed from O-atoms at point (2), where (2) may in reality be the location of the cold trap (refer to figure 3). Then, by the conservation of mass

$$[O_2]_x = [O_2]_o + (1/2) [O]_o [\exp (-vX/D)] \quad (6)$$

and $[O]_x = [O]_o \exp (-vX/D) \quad (7)$

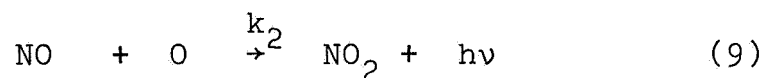
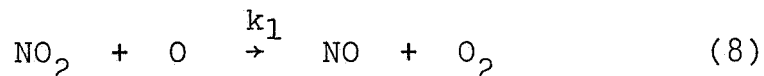
where $[O_2]_x$ = concentration of O_2 at any point (X).

$[O_2]_o$ = concentration of O_2 at point (1) upstream where $\exp (-vX/D)$ approaches zero.

$[O]_x$ = concentration of O-atoms at point (X).

$[O]_o$ = concentration of O-atoms where $\exp (-vX/D)$ approaches zero.

The one step NO_2 titration method utilizes the following reactions:



NO_2 is added until the afterglow is extinguished. Since reaction (8) is much faster than (9) all added NO_2 is converted to NO so that $[NO] = [NO_2]_{\text{added}}$. Incorporating this into the differential rate expression for (9) one gets

$$\frac{d[h\nu]}{dt} = k_2 [NO] [O] = k_2 [NO_2] [O]. \quad (10)$$

Introducing expression (7) into equation (10) it becomes:

$$\frac{d [hy]}{dt} = k_2 [NO_2] ([O]_o - [NO_2]) [1 - \exp(vX/D)]. \quad (11)$$

$\frac{d [hy]}{dt}$ is set equal to zero and one finds that $[O]_o = [NO_2]_{\text{added}}$ at

extinction of the light intensity. At this point it should be apparent that this titration gives the upstream concentration $[O]_o$. Thus if one wants the true oxygen atom concentration $[O]_x$ one must titrate to find $[O]_o$ and then calculate $[O]_x$ from equation (7).

The two step titration method also uses reactions (8) and (9) but the procedure is different. In this method NO_2 is added to maximize the light intensity, $\frac{d [hy]}{dt}$, followed by a measure of NO

that must be added to equal that intensity. As before, the rate equation for reactions (8) and (9) is

$$\frac{d [hy]}{dt} = k_2 [NO_2] ([O]_o - [NO_2]) [1 - \exp(-vX/D)].$$

Then to maximize the light intensity, differentiating and setting equal to zero one sees that

$$\frac{d}{d [NO_2]} \left[\frac{d [hy]}{dt} \right] = k_2 ([O]_o - 2[NO_2]) [1 - \exp(-vX/D)]. \quad (12)$$

From this follows that $[O]_o = 2 [NO_2]_{\text{added}}$ at the maximum.

$$\text{Thus } \left. \frac{d [hy]}{dt} \right|_{\text{max}} = \frac{k_2 [NO_2] [O]}{2} = \frac{k_2 [O]_o ([O]_o - 1/2 [O]_o)}{[1 - \exp(-vX/D)]^{-1}}$$

$$\text{or } \left. \frac{d [hy]}{dt} \right|_{\text{max}} = \frac{k_2 [O]_o^2 [1 - \exp(-vX/D)]}{4}$$

In the second step one adds NO to equal this maximum intensity.

It is found that

$$\begin{aligned} \frac{d[\text{hy}]}{dt} \Big|_{\text{max}} &= k_2 [\text{NO}] [\text{O}]_0 [1 - \exp(-vX/D)] \\ &= k_2 [\text{O}]_0^2 [1 - \exp(-vX/D)]. \end{aligned} \quad (13)$$

This shows that upon completion of the titration the $[\text{NO}]_{\text{added}} = [\text{O}]_0/4$. Thus again we see that the titration will not give the true oxygen atom concentration at a point where back diffusion is involved.

Experimentally one may easily set up a system where back diffusion will be a problem using the Hertz equation as a guide. One may then place his light detector at any point (X) and determine $[\text{O}]_0$. If the detector is moved toward the cold trap the intensity will fall off as $\exp(-vX/D)$. One can not explain this intensity decrease as a consumption of O atoms by NO or a decrease in total pressure as one may easily calculate.

Determination of Recombination Efficiency (γ)

The fraction of oxygen atoms lost on collision with a metal surface (γ) is determined from the decay curve of light intensity as a function of time. The apparatus (figures 1 and 2) is operated as a steady-state flow system with the decay occurring when the oxygen atom supply to the reaction vessel is interrupted by turning off the discharge. If the system is clean and no metal specimen is present, the oxygen atoms will effuse out of the reaction vessel through the hole (figure 1) rather than suffer any significant loss due to recombination in the vessel. Since the mean free path of the atoms is much greater than the dimensions of the vessel the effusion rate corresponds to the simple kinetic formula,

$$N/n = cA/4 \quad , \text{ where} \quad (14)$$

N = number atoms per second passing through the hole of area A ,

n = atom density per cm^3 in the vessel,

c = average velocity of the atoms in cm/sec , and

A = area of the hole in cm^2 .

The decrease in the number of oxygen atoms, $-d(O)/dt$, from the total number, (O) , is $n_0 cA/4$. Since $(O) = n_0 V$, where V is the volume of the vessel, one may state the above relation as

$$\frac{-d(O)/dt}{(O)} = \frac{n_0 cA/4}{n_0 V} = \frac{cA/4}{V} \quad (15)$$

This, after rearrangement and integration is

$$\ln (O)_1/(O)_2 = (cA/4V)(t_2-t_1). \quad (16)$$

Thus by a usual definition of a decay half-life this gives

$$\ln 2 = (cA/4V)t_{1/2}^O. \quad (17)$$

From the above, one should notice that varying the hole size (A) changes effusion rate of decrease in oxygen atom concentration which is proportional to the intensity of chemiluminescence observed. Since this decay is exponential, its half-life ($t_{1/2}^O$) can be measured. Note also that the steady state pressure in the flask increases inversely with the hole size. In Table II are shown the decay times ($t_{1/2}^O$) and steady state pressures for a given throughput of gas and fixed volume.

Table II

Decay half-lives of light intensity and steady state pressure for a 6 liter flask with a throughput of approximately 4×10^{14} particles per second.

Area (cm^2)	$t_{1/2}$ (seconds)	Pressure (torr x 10^6)
1	0.38	1.0
0.38	1	2.6
0.25	1.52	4
0.2	1.9	5
0.1	3.8	10.

The pressure readings on the ion gauge will not be entirely correct since the oxygen oxidizes parts and inaccuracies result. To avoid this a check is made using argon.

The vessel being used experimentally has a volume of six

liters with the area of the hole variable. The half-life of the O-atoms in the vessel (the half life of light intensity) is then

$$t_{1/2}^o = \frac{V \ln 2}{(cA/4)} = \frac{(6 \times 10^3)}{(1.6 \times 10^4)A} = \frac{0.38}{A} \text{ sec} \quad (18)$$

since the pumping speed corresponding to O-atoms effusing out of the flask through a one square centimeter hole is $(6.3 \times 10^4)(1)/4$ or $1.6 \times 10^4 \text{ cm}^3/\text{sec}$.

For a metal surface of area A_m introduced into the system and destroying oxygen atoms with an efficiency of γ , the above analysis must be modified such that if equation (17) is set equal to equation (18) one gets

$$\left(\frac{cA_o}{4V}\right) t_{1/2}^o = \left(\frac{cA_o}{4V} + \frac{cA_m \gamma}{4V}\right) t_{1/2}^m \quad (19)$$

or $t_{1/2}^o = (1 + \gamma A_m/A_o) t_{1/2}^m$ which is

$$\text{equivalent to } \frac{A_o}{A_m} = \frac{\gamma}{(t_{1/2}^o / t_{1/2}^m) - 1} \quad (20)$$

Thus if one measures a decay half-life without a metal sample present ($t_{1/2}^o$) which corresponds to an effective hole area (A_o) as well as a $t_{1/2}^m$ for a known A_m one may use equation (20) or figure 14 to find a precise γ . Equation (20) is plotted in figure 4.

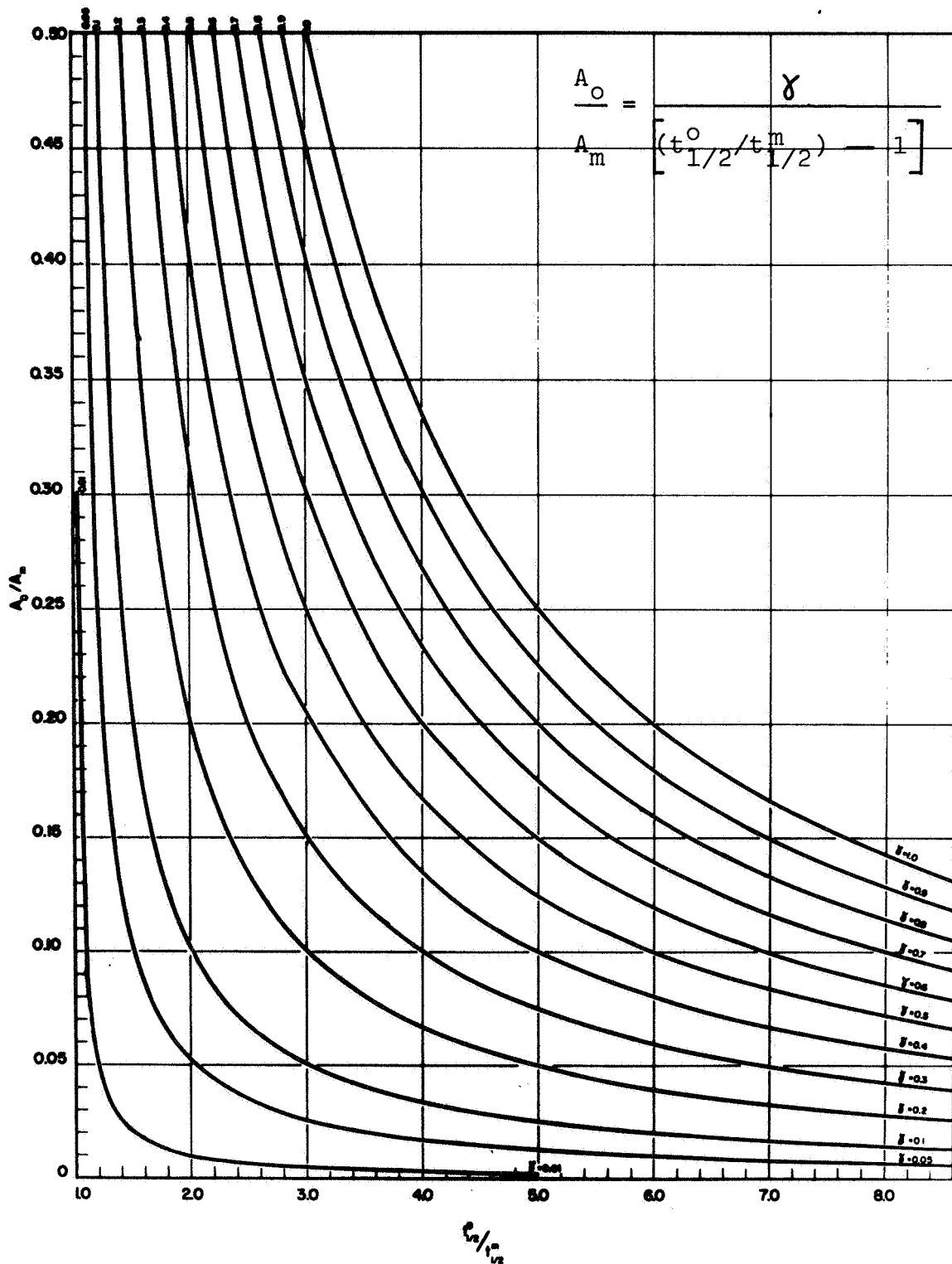


Figure 4.