AFOSR Scientific Report
AFOSR-68-0883

(1)

TECHNICAL REPORT

SURFACE RECOMBINATION EFFICIENCIES IN FLOWS CONTAINING STEP-FUNCTION INCREASES IN ATOMIC OXYGEN

By: A.L. Myerson

CAL No. AF-2033-A-1

Prepared for:

U.S. Air Force Office of Scientific Research
of the Office of Aerospace Research
Arlington, Virginia 22209

Research monitored under the technical
supervision of Mr. Milton Rogers (SREM), AFOSR

FINAL TECHNICAL REPORT
Contract No. AF 49(638)1487
Project No.
March 1968

CORNELL AERONAUTICAL LABORATORY, INC.
OF CORNELL UNIVERSITY, BUFFALO, N. Y. 14221

AFOSR-68-0893

CORNELL AERONAUTICAL LABORATORY, INC.
BUFFALO, NEW YORK 14221

SURFACE RECOMBINATION EFFICIENCIES IN FLOWS CONTAINING STEP-FUNCTION INCREASES IN ATOMIC OXYGEN

FINAL TECHNICAL REPORT
CAL REPORT NO. AF 2033-A-1
CONTRACT NO. AF 49(638)1487
MARCH 1968

Prepared For:
U.S. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
OF THE OFFICE OF AEROSPACE RESEARCH
ARLINGTON, VIRGINIA 22209

PREPARED BY: A. L. Myerson
A.L. Myerson

APPROVED BY: J. Gordon Hall
J. Gordon Hall, Head
Aerodynamic Research Department

FOREWORD

The research reported herein was sponsored by the Air Force Office of Scientific Research of the Office of Aerospace Research under Contract AF 49(638)-1487 and was monitored under the technical supervision of Mr. Milton Rogers (SREM), AFOSR. The work was performed by the Aerodynamic Research Department of the Cornell Aeronautical Laboratory, Inc. This technical report describes research performed during the period 1 December 1964 to 31 December 1967. Since this contract was essentially a continuation of the previous Contract No. AF 49(638)-782, much of the work herein described is based on the background obtained during that earlier period, although a final report was issued at the end of that period. A list of reports and papers resulting from these contracts is appended to this report.

The author wishes to acknowledge the excellent technical assistance of Mr. J. L. Rasinski in carrying out these experiments and the valuable discussions with, and suggestions of, Dr. Sang-Wook Kang.

ABSTRACT

A study has been made of the initial interaction of atomic oxygen with various metals in steady flows which provide a step-function increase, or pulse, in the atom concentration. The observations have been made by means of thin-film resistance thermometry. The results are presented under three categories as follows:

Surface recombination efficiencies (γ) have been measured as a function of exposure time in pulses of oxygen atoms over various metals in Oseen flows. Cylindrical, circumferentially-coated, thin-film resistance thermometers were used to determine the rate of heat transfer. The relationship between the surface and free stream concentration of oxygen atoms was obtained by means of the mathematical analogy between heat and mass transfer. It was possible to use relatively high partial pressures of atomic oxygen and carrier gas (1% atomic oxygen in a flow pressure of 4 to 6 mm Hg of an Ar-O_2 mixture) which are important to the accuracy of the measurements of many of the parameters involved. Under these conditions, the dependence of γ on exposure time was obtained as a function of time for periods up to several seconds. Each of the metals investigated exhibits a markedly different time history of γ during the period of initial gas-solid interaction, and the γ of each metal eventually reaches a final but different stable-state value. The final values are 0.12, 0.03, 0.017, 0.0085, 0.007, and 0.005 for Ag, Cu, Fe, Ni, Al, and Au respectively, which values are generally lower than those previously reported. Reasons for these differences are presented.

Atom concentrations have been measured in pulsed or step-function flows of atomic oxygen. This has been accomplished by employing thin-film heat transfer gauges along with the NO_2 titration technique, which normally makes use of a visual radiation end point. In the present work, the gauges have been used to detect the atoms remaining after various known fractions have been removed by NO_2. A curve results which can be extrapolated to obtain an accurate end point. A number of determinations made in this way are presented. In addition, it is shown how this technique can be applied to the determination of homogeneous atom decay rates.

The rate at which the recombination heat transfer on a newly exposed metal reaches its peak in a step-function flow of atomic oxygen has been interpreted in terms of the rate at which the catalytic oxide initially forms. The rates have been measured for two different series of heat transfer-time histories involving Ag, Cu, Fe, Ni, and Au. In addition, a relationship has been shown to exist between the rate of oxidation and the heat of sublimation of the metal.

TABLE OF CONTENTS

LIST OF SYMBOLS

$\bar{D}_{12}$	diffusion constant for O atoms into an Ar-O_2 mixture (cm^2 sec^{-1})
E_{act}	energy of activation (kg cal mole^{-1} °C^{-1})
F_{Ar-O_2}	flow rate of Ar-O_2 mixture (mole sec^{-1})
γ	surface recombination efficiency or fraction of atoms colliding with a surface which recombines
G	mass rate of atoms recombining on surface (g cm^{-2} sec^{-1})
ΔH_s	heat of sublimation (cal g-mole^{-1})
$M_{[O]}$	atomic weight of oxygen
M_{Ar-O_2}	molecular weight of Ar-O_2 mixture
m_s	mass fraction of O atoms in gas, at surface
m_∞	mass fraction of O atoms in gas, in the free stream
Nu	Nusselt number
Nu_m	mass transfer Nusselt number (=Sh)
$P_{[O]}$	partial pressure of atomic oxygen in the free stream (mm Hg)
P_{tot}	total pressure of free stream (mm Hg)
$\dot{q}$	heat-transfer rate (cal cm^{-2} sec^{-1})
R	gas constant
ρ_{tot}	total density of free-stream flow (g cm^{-3})
Sh	Sherwood number = Nu_m
θ	angle from direction of axial flow
t	time
$\tau_{1/e}$	time for $\dot{q}$ to reach $1/e$ of maximum
u_∞	linear flow velocity at gauge coordinate (cm sec^{-1})

I INTRODUCTION

The research described in this report is the result of an effort to study any unique features which might exist for oxygen atom-metal interactions during initial contact, in contrast to their steady-state behaviour. The principal characteristics studied were the changes that occurred in surface recombination efficiency, γ, during the initial reaction between the atom and the metal film as brought about by imposing a step-function increase, or pulse, in oxygen atom concentration on an argon-molecular oxygen flow. The results and their interpretation have been divided into three sections, in the following discussion, which describe: (1) the effect of the duration of initial exposure to oxygen atoms on the value of γ, for a given metal, (2) the manner in which a critical parameter, the oxygen-atom concentration during the pulsed atom flow, was measured and (3) an interpretation of the exposure-dependent values of γ in terms of the rate of surface oxidation.

II. EXPOSURE-DEPENDENT SURFACE RECOMBINATION EFFICIENCIES IN FLOWS CONTAINING STEP-FUNCTION INCREASES IN OXYGEN ATOM CONCENTRATION

Prior to observations of surface catalyzed atom recombination in steady flows containing step-function increases, or pulses, in atomic oxygen,[1, 2, 3] all such studies, including measurements of the efficiency γ, were made under steady-state conditions.[4, 5]

Under these conditions, γ was not determined until the parameters measured had reached limiting values, a process requiring many minutes and usually a significant fraction of an hour of exposure of a metal to atomic oxygen. However, as was shown qualitatively in previous papers,[1, 2] most of the interesting changes in surface chemistry which actually determine both the initial and ultimate or stable-state value of γ, all take place in the first several hundred milliseconds of metal-oxygen atom interaction. It is, therefore, one of the purposes of the paper to present the absolute values of γ, measured by thin-film resistance thermometry, as a function of exposure-time during this early "conditioning" exposure to atomic oxygen. This has been done for a number of metals each of which is shown to have its own unique time history of γ during this initial gas-solid interaction. A final or stable-state γ of the metal is then presented and an attempt made to correlate these values of γ with the state of oxidation of the metal.

A second purpose of this paper is to present the new or unique aspects of the theoretical and experimental approach used to obtain some of the fundamental parameters necessary for the calculation of γ. The only previous measurement[3] of γ in step-function flows was made at the stagnation line of a cylinder (or sphere) which entailed a theoretical solution valid only for low diffusion Reynolds numbers. The present research makes use of a circumferential thin-film resistance thermometer which measures the average rate of recombinative heat-transfer, $\dot{q}$, around a cylinder. This makes feasible the use of much higher (by almost an order of magnitude) pressures both total and atomic, which yield higher $\dot{q}$'s from which γ can then be calculated.

An important sidelight of this research is the quantitative evidence found for the transfer of energy from excited species to the catalytic surface when 100% oxygen is used as the flow gas, as has been the case in most previous studies of the surface recombination of atomic oxygen. This undesirable effect has been eliminated here, for heterogeneous phenomena, by the method reported by Clyne, McKenney, and Thrush[6] (CMT) for homogeneous studies, viz., the use of oxygen diluted by argon.

The technique and theory employed and the observations and their interpretations are described in this section.

A. Experimental

The basic apparatus used in this research has been described previously.[2] However, since several important changes have been made a schematic diagram is shown in Fig. 1.[*] The principal change was in the probe itself on which were fired narrow circumferential bands of platinum (1.5 mm wide) covering some 270° of the pyrex cylinder circumference, instead of the stagnation line gauges formerly used. These were coated with fired titanium oxide sometimes reinforced with a baked silicone resin film. The foils, or evaporated films in the case of the aluminum, covered several mm above and below the band. The fired silver leads also were insulated by the baked silicone mentioned above. The probe was flush mounted into the pyrex tube by means of teflon holders, since it was found that any cavities affected the results quantitatively.

While the platinum and titanium dioxide were only 0.1 μ thick as before, the foils were as thick as 1 μ except for the very thin coating of evaporated aluminum. The thicker foil was found to have no effect on the response-time involved in these experiments.

A rigorous quantitative basis was necessary for these determinations. The flow parameters which required accurate measurement were the following: $p_{[O]}$ the partial pressure of atomic oxygen; p_{tot} the total pressure, and F_{Ar-O_2}, the molal flow rate. The most difficult of these measurements was that of the atomic oxygen. This was accomplished by

---

[*] A detailed drawing is shown in the Appendix in Fig. A-1.

a variation of the NO_2 titration technique which, since it will be described elsewhere in this report in detail, is indicated here only in brief outline. The atomic oxygen was reacted with various flows of NO_2 let in at the point indicated in Figure 1. However, instead of conventionally following the afterglow, the atoms remaining were detected by a catalytic thin film gauge as previously described. This provided a dependable and sensitive measure for the end point. The small flows of NO_2 measured were of the order of 10^{-5} to 10^{-6} mole sec^{-1}.

The total pressure was measured by means of a pneumatic pressure transmitter which provided, on a mercury manometer, magnified values for the pressure region of interest. The molal flow rate was determined by observing the pressure differential across a capillary and relating it to volume flow by calibrating the differential against the pressure rise in an evacuated reservoir of known volume. The gas used throughout these studies for the final determination, a mixture of 10% oxygen in argon, was commercially obtained and consisted of ultra-high purity components only.

The measurement of $\dot{q}$, the heat-transfer rate, was carried out as previously described. Summarizing briefly, the thin-film gauges were calibrated by measuring their resistance as a function of temperature when, in protective containers, they were immersed in thermostatically controlled water baths. During observations, an electronic analog network converted the changing resistance directly to heat-transfer rates. The temperature coefficient of resistance of the gauge and an electronically-produced standard of $\dot{q}$ were used to calibrate the oscilloscope deflection in terms of absolute values of heat transfer.

A number of refinements were made in the radiofrequency (RF) pulsing apparatus which improved the reproducibility of atom production. These included plastic spacers placed between the ring electrodes and the glass to maintain circular symmetry, close control of room temperature and finer measurements of RF input voltage. It was shown, in the course of the investigation, that the effect of temperature on the partial pressure of atomic oxygen was not negligible, being of the order of several tenths of a percent per °C. This observation became possible only when the determination of $\rho_{[O]}$ was improved to the extent that the percent error was 3 to 5%. The accuracy of the pressure and flow parameters measured was approximately ± 1% while that for $\dot{q}$ was ± 2 to 3%. A typical determination of γ vs t was made by first evacuating (usually to 10^{-6} mm Hg) and outgassing the system containing the probe with its freshly applied 360° band of pure-metal foil previously washed and degreased. The band of foil overlapped the thin-film by several mm on top and bottom and the probe was placed at the location where the NO_2 jet is indicated in Fig. 1. The mixture of 10% oxygen in argon was then allowed to flow for several minutes at a constant pressure and velocity. The step-function of atomic oxygen was imposed on the flow by pulsing the RF field for several hundred milliseconds resulting in a trace such as that illustrated by Fig. 1 for copper. This trace provided a record of the initial $\dot{q}$ history of the metal over a several hundred millisecond period. Additional pulses separated by intervals of several minutes, were then applied until it was evident that a stable-state value of $\dot{q}$ has been obtained.

B. Results and Discussion

The calculations of γ from the measurements described herein call upon the mathematical analogy between heat and mass transfer as applied to the case of Oseen flow around a cylinder. If the mass fraction of atomic oxygen m_s present in the gas at the surface of the circumferential thin-film gauge were known, γ could be simply calculated from first principles of first-order surface kinetics[7, 8]

$$\gamma = \frac{G}{\rho_{tot}\left(\frac{M_{[O]}}{2\pi RT}\right)^{1/2}\left(\frac{M_{Ar-O_2}}{M_{[O]}}\right)m_s} \qquad (1)$$

where the symbols are defined as follows:

G = rate of atom recombination on catalytic metal surface in g cm^{-2} sec^{-2}

$M_{[O]}$ and M_{Ar-O_2} = atomic and molecular weights of atomic oxygen and the $Ar-O_2$ mixture, respectively

ρ_{tot} = total pressure of the flow mixture of $Ar-O_2$

Since it is not feasible to measure the atom mass fraction at the surface, m_s . whereas it is possible to measure the mass fraction in the free stream, m_∞ . the problem becomes one of determining the relationship between m_s and m_∞ . This is given by the following expression which is simply a definition of the mass transfer Nusselt number Nu_m, usually known as the Sherwood number, Sh

$$m_s = m_\infty - \frac{Gd}{Sh\,\rho_{tot}\,D_{12}} \tag{2}$$

where d = probe diameter

ρ_{tot} = total mass density of the free stream

D_{12} = diffusion constant for atomic oxygen into the Ar-O_2 mixture

While Sherwood numbers are not available as such, for the case at hand which is that of average mass-transfer around a cylinder, an excellent group of determinations is available for heat-transfer Nusselt numbers Nu under corresponding conditions of average heat-transfer around a cylinder.[9] By virtue of the mathematical analogy between heat and mass transfer,[10] Nu and Sh are numerically identical. The appropriate value of Sh for a given determination could then be found as a function of the Reynolds number, Re, for the particular flow conditions used. Values of Re in these studies fall between 5 and 10.

The values for D_{12} were calculated with the aid of the Brokaw Alignment Charts[11] and are accurate to within a few percent so that the diffusion constant is not the limiting factor in the accuracy of these determinations. Values for D_{12} were first calculated for O atoms into pure oxygen and found to check within a few percent of the values determined experimentally[12] using EPR.

The other parameters were determined as described in the experimental section. The mass rate of atomic recombination, G, was calculated from the measurement of q; m_∞ from the measured flow of atomic oxygen, as derived from the modified NO_2 titration; ρ_{tot} , the total pressure, from the direct transmitter measurement and F_{Ar-O_2} , the total molal flow rate, from the flow calibration experiments. Corrections or adjustments were made for the following factors:

1. While the measurements made were to apply to the average value around a cylinder (Sh for 360°), the gauge could not be made to cover more than some 270°. A correction was made by measuring the $\dot{q}$ profile as a function of the angle, θ, using a stagnation-line gauge on a cylindrical probe. The measured value of the average $\dot{q}$ for the circumferential gauge could then be readily extrapolated to 360° to allow for the angle not covered by thin-film. A typical $\dot{q}$-θ profile is shown in Fig. 2.

2. It was found that the atom concentration in the flow tube was not quite uniform in the radial direction. A profile of $\dot{q}$ $(\propto m_{\infty})$* as a function of radial distance in the flow tube was obtained by means of the circumferential probe. From this profile and the known average value of m_{∞}, a correction (~10 to 20%) was applied which was dependent on the distance from the tube axis at which the circumferential gauge was used.

3. In calculating Re, a knowledge of the axial flow velocity profile is necessary while the velocity available from volume flow is the average over the entire diameter. The necessary information was obtained from the parabolic velocity profile, the symmetrical existence of which was checked experimentally using the cooling of the thin-film probes herein employed, as the diagnostic technique.

The γ experiments were initially carried out with 100% O_2 as the flowing gas, as have been all previous studies (both steady- and non-steady state) in which the γ for atomic oxygen was measured. After the experimental procedure had been brought to its optimum accuracy, as described in the experimental section, it became clear that evidence was present for excess heating of the gauge, above that attributable to recombination. This manifested itself in measurements with silver which has the highest γ known. The calculation of γ used herein is quite sensitive, by virtue of equation (2), to the value used for G when γ, and hence G, are high.

---

*This follows from equations (1) and (2).

Thus, in the case of silver, it was found that σ was too high to permit the substraction which is required by (2) to yield a positive value. Since it is well known that discharges form excited molecular oxygen, O_2^* ($^1\Delta_g$) this had originally been regarded as a likely source of the spurious heating

It was at first believed[2, 3] that the simultaneous decrease of O atoms and catalytic heating on the gauge, as the NO_2 flow rate was increased, was evidence for the existence of heating due only to recombination. However, if the excited oxygen were de-excited in the gas-stream when NO_2 and the consequent reaction products were present, this previous conclusion would be invalid. It was then noted that CMT were able to show that O_2^* and its spurious kinetic effects could be eliminated by using mixtures rich in argon instead of pure O_2. Atom calibrations and $\dot{q}$ measurements were therefore carried out with a mixture of 10% O_2 in Ar and compared with the results obtained with 100% O_2. It had been noted earlier that, with 100% O_2, the excess heating increased with RF voltage. This could be ascribed to increased formation of O_2^*. A quantitative study of this effect was made by measuring the ratio $\dot{q}/p_{[O]}$ (recombination heating per atom) as a function of voltage since this should be constant in the absence of non-recombinative heating from excited species. A plot of the results with pure O_2 is seen in Fig. 3a. It was never possible, under any conditions, to find a voltage sufficiently low to allow this ratio to become constant. On the other hand, with a 90% - 10% mixture of Ar-O_2, a plot such as that shown in Fig. 3b was obtained. As can be seen, there is no problem in obtaining values for $\dot{q}/p_{[O]}$ which level out, even at high voltages, in corroboration of the results of CMT.

All measurements were made, therefore, with the Ar-O_2 mixture. The curves of γ vs exposure time to the atom pulse are shown in Fig. 4. They were obtained from a series of traces resulting from pulses of 300 msec duration, starting with previously unexposed metal* and repeating the pulses at regular time intervals until γ reached a constant or stable-state value. The data† corresponding to the stable-state values of γ are given in Table I.

Table I

DATA FOR STABLE-STATE VALUES OF γ

Metal	p_{tot} (mm Hg)	$p_{[O]}$	$\dot{q}$ (cal cm^{-2} sec^{-1})	Sh	u_{∞} (cm sec^{-1})	γ
Ag	5.73	0.0838	0.0435	1.91	397.5	0.110
Cu	5.73	0.0838	0.0351	1.91	397.5	0.031
Au	5.66	0.0856	0.0143	1.92	410.5	0.0047
Fe	5.66	0.0856	0.0303	1.92	410.5	0.0180
Ni	5.66	0.0856	0.0210	1.92	410.5	0.0085
Al	5.66	0.0856	0.0184	1.92	410.5	0.0068

It is clear from these traces, that the formation of the stable-state catalytic oxide is a complex matter. In half the cases, over three seconds total exposure to atomic oxygen is required to form the final oxide. And in no case is a final γ high compared to that of silver, in line with the theory pertaining to silver presented in a previous paper[1] and contrary to some of the earlier values for the γ of copper. The reasons for this disagreement will be discussed shortly in conjunction with Table II.

In all cases except Ni, γ decreases from an initial peak value before going on to form its final stable-state value. Even in the case of Ni, there is an early change of slope which may be evidence of an unresolved peak. Remembering from eq. (1), that γ is a monotonic function of $\dot{q}$, part of the initial $\Delta\gamma$ may be attributed to the initial heat of formation of the oxide, e.g., Ag_2O, at the surface. However, where the area under

---

*All metal foils had to be exposed, of necessity, to molecular oxygen before the atom pulse was generated.

†The complete data for these results are given in Table A-I of the Appendix.

the curve is great, e.g., Ag, Cu and especially Al, this involves much more total heat evolution ($\Delta H_{tot} = \int \dot{f}\, dt$) than can be accounted for by the formation of a few layers of silver or other oxides.* The only possible source of so much energy is recombination and the most likely explanation for why it dies out is that the catalytic oxide responsible is an unstable one and is superseded by the final more stable one.

The final-stable-state values obtained for γ are presented in Table II and compared with data previously published.

Table II

SURFACE RECOMBINATION EFFICIENCIES (γ) FOR OXYGEN ATOMS

	Metals			Oxides	
	Greaves and Linnett[13]	Hartunian Thompson & Safron[3]	Myerson	Greaves and Linnett[13]	Dickens and Sutcliffe[14]
Ag	0.24	0.15	0.116		
Cu	0.17	0.15	0.03	0.043 (Cu^{+2})	0.11
Fe	0.036		0.017	0.0052 (Fe^{+3})	0.0085
Ni	0.028	0.04	0.0085	0.0089	0.0015
Al		< 0.01	0.007	0.0021	
Au	0.005		0.005		

The value given for Ag represents an average of 10 determinations. Those of Greaves and Linnett[13] and Dickens and Sutcliffe[14] were determined by a steady-state technique while the other[3] applied step-function or pulse techniques. It will be seen that the most significant difference is that the present results for metals are, in general, lower than those obtained previously. It is believed that the principal reason for the difference is the extra heating produced by excited oxygen, as previously disucssed, which deposits varying amounts of heat on a metal, dependent

---

*A typical calculation illustrative of this point may be found in Ref. 2.

on the nature of the metal or its oxide.[15] It is perhaps significant that agreement is better in the comparison of the present results, which are believed to represent the stable-state oxide, with those obtained previously for oxides, in spite of the fact that very small amounts of heat are involved. It may well be that the contribution of excited oxygen is minimized by the use of the bulk oxide in the steady-state work, as just mentioned.

Other factors which may be involved in the difference, insofar as comparison with step-function data are concerned, are the inherent capacity for more accurate measurements of the parameters involved herein, as provided by the higher pressures and the modified technique for measuring oxygen atom concentrations.

C. Conclusions

The early history of γ, the surface recombination efficiency, has been studied as a function of exposure time to atomic oxygen, by observations made under conditions of relatively high pressures and by using small percentages of oxygen in argon. It is necessary to apply the analogy between heat and mass transfer to determine the relationship between surface- and free-stream atom concentrations.

III. THE DETERMINATION OF OXYGEN ATOM CONCENTRATIONS IN PULSED ATOM FLOWS

This section of the report describes the determination of the gas-phase oxygen atom concentration through the application of a thin-film gauge, as used herein, to the NO_2 titration technique. In addition, it has been shown that the gauge can be used to measure the rate of disappearance of atomic oxygen in homogeneous reactions such as $O + O_2 + O_2 \rightarrow O_3 + O_2$. This is in contrast to the usual function of this gauge as a detector of gas-surface phenomena as illustrated throughout this program.

The requirements for measuring atom pulses of short duration (0 to 300 msec) differ radically from those for steady flows in which studies of atom concentration and recombination have previously been made. It is not possible to run the discharge continuously with the power and electrode configuration involved and the linear flow rates are, in general, faster than those used in steady flows because of the need to maintain a sharp atom front. These factors, along with the pulsed nature of the atom flow, preclude accurate use of the afterglow visual titration methods. Here measurements have been made, during the pulsed flows previously described, of the free-stream oxygen atom concentration using, as a basis, the linear relationship between surface-recombination heat transfer and free-stream atom concentration.

The many determinations of oxygen atom concentrations in flow systems have all been made under conditions of continuous flow, except for the pulsed flow studies of Hartunian.[3] The latter and many of those using continuous atom flows have made use of the NO_2 titration technique for this purpose. However, while the titration reaction

$$O + NO_2 \rightarrow O_2 + NO \qquad (I)$$

has been used in the present case, it has been found that a necessary improvement* in accuracy could be achieved by using the thin-film probes developed herein, in place of the radiation end point method. By applying the rapid response of the thin-film thermometer to the detection of the atoms remaining downstream of a point where a known extent of reaction (I) had taken place, a method was evolved that provided reliable and accurate results.

With the establishment of the gauge application described above, it became relatively easy to develop a means of measuring the rate of loss of atomic oxygen in gas-phase reactions such as

$$O + O_2 + M \rightarrow O_3 + M \qquad \text{(II)}$$

This involves only a measurement on the atomic probe heating at two different points downstream of the electrodes, and the free-stream velocity at the gauge location. Preliminary observations of this type of measurement were made before the elimination of O_2^* through the use of Ar-O_2 mixtures and prior to a number of other changes necessary for the final determinations reported. Hence, no quantitative results for homogeneous rates are reported.

A. Experimental

The basic components of the apparatus used in this work, such as the probe and flow system, are essentially the same as those described in Section II so that the configuration of the system used to perform the present experiments also is shown schematically in Figure 1. A doughnut-shaped spray-head with four small holes from which NO_2 was allowed to flow upstream, was mounted at a point in the flow tube at which the concentration was to be determined. The detailed apparatus used for NO_2 calibration is shown schematically in Figure A-2 of the Appendix. The very small flows of NO_2 were measured precisely by means of a separate system. The NO_2 flow was calibrated by measuring its pressure drop across a capillary 6" in length and 0. 017" in diameter, and relating the

---

*This improvement was mandatory for the measurements of γ previously described.

drop to the flow rate. The flow itself was measured by following the pressure change in a fixed volume. Sensitive pneumatic transmitters with stainless steel diaphragms were used throughout to measure pressures. The serious errors introduced by manometer fluids were thus completely eliminated.

The thin-film probe was placed 8 cm downstream of the NO_2 jets and provided a measure of the atom concentration after removal of a given fraction by NO_2. In an actual experiment, the NO_2 flow was first stabilized at a desired value. The atom pulse or step function was then formed by rapid application of the radiofrequency field and a value obtained for $\dot{q}$ corresponding to $\rho_{[O]}$ at the probe. Since there exists a slow drift of the efficiency (∂) of the silver in the presence of NO_2 after initial conditioning, all values of $\dot{q}$ were referred back to a standard $\dot{q}$ represented by q_0. This was accomplished by observing $\dot{q}$ for a standard pulse of $\rho_{[O]}$ (as controlled by a given and constant voltage) at regular intervals during any series of observations.

The experimental configuration was altered if one wished to determine the time required for a given loss of $\rho_{[O]}$ between two points in the flow. An observation of $\dot{q}$ was first made with a probe in the upstream position (where the NO_2 inlet is indicated). Then the upstream probe was removed and a measurement of $\dot{q}$ made with a probe in the downstream position, under identical physical conditions. The possible interpretation of such data will be discussed in the succeeding sections.

B. Results and Interpretation

1. Determination of $\rho_{[O]}$ in an Ar-O_2 Mixture

The determination of $\rho_{[O]}$ in the fast, pulsed flow of 10% O_2 in Ar cannot be accomplished with any desirable degree of accuracy by visual observation of the end point. On the other hand, the titration curves which will be described here provide a high degree of accuracy and dependability. The measurement of $\rho_{[O]}$ corresponding to a given set of gas parameters and RF field (voltage) consists of a series of observations of $\dot{q}$, each made after establishing a different and known flow rate of NO_2 in the system of Figure 1, as described in the experimental section. This procedure results in a series of traces of the type shown in Figure 5. From such a series, a plot of $\dot{q}_{NO_2}/\dot{q}_0$ as a function of F_{NO_2} can be obtained as shown in Figure 6. Here $\dot{q}_{NO_2}/\dot{q}_0$ represents heating due only to the oxygen atoms remaining* after removal of a given fraction by the flow of NO_2 whose rate is plotted on the x-axis. The end point is reached when the rate of change of $\dot{q}_{NO_2}/\dot{q}_0$ with respect to F_{NO_2} first attains a slope of zero.

It will be noted that the traces of Fig. 5, although for conditioned silver, show a decreasing (but leveling) trend for $\dot{q}$ with time. It was sometimes found that this condition began to manifest itself after the RF generator had been used to provide many pulses in succession. This situation typically occurred in the case of the NO_2 titration where many pulses were run before beginning observations and where the presence of NO_2 appeared to amplify the slope-effect in question. The decreasing $\dot{q}$ and hence $\rho_{[O]}$ during a pulse can be attributed to a decreasing, gas-coupled, RF field produced by the generator during the pulse. This drift of $\dot{q}$ had no effect on the end-point interpretation, since the same part of a pulse, viz., that just after the initial maximum, was always used for the end-point plot. Furthermore, $\dot{q}_{NO_2}/\dot{q}_0$ was found to level off to its minimum at the same F_{NO_2}, for any consistently chosen part of the pulse. The early pulses (e.g., the first 10 or so) for a given series showed constant $\dot{q}$'s, as illustrated by the flat portion for Cu in Fig. 1, and provided the traces used for the γ-measurements of Section II.

The plotting of $\dot{q}$ rather than $\rho_{[O]}$ is justified by the relationship

$$\dot{q} \doteq \left[\frac{2\gamma Z}{1-\gamma/2}\right] \cdot \left[\frac{(1-\gamma/2)\, Sh\, \rho D_{12}}{(1-\gamma/2)\, Sh\, \rho D_{12} + 2\gamma Z d}\right] m_{\infty} \qquad (3)$$

where $Z = \rho_{tot} \left(\frac{M_{[O]}}{2\pi RT}\right)^{1/2}$

---

*In this case the noncatalytic or convective heating is also included in $\dot{q}$ and it is normalized by dividing by q_0 (= $q_{standard}$) as described previously.

which follows from equations (1) and (2) and which shows that, for a given set of conditions, $\dot{q}$ is linear in m_∞, the free stream atom concentration, since all quantities within the bracket are independent of m_∞.

The titration curve values are modified by two major factors. One of these is the gradient of oxygen atom concentration in the concentration boundary layer around the cylindrical gauge. This in principle does not modify the linear relationship of the variables. The other is the effect of further recombination of atomic oxygen, with the NO produced during the $O + NO_2$ reaction acting as a more effective third body than either O_2 or Ar. This results in a curved-line titration curve as was obtained by Westenberg and Haas[16] in a steady state measurement of $\rho_{[C]}$ by EPR. In Figure 7 are shown typical curves calculated for the purpose of illustrating the successive effects of gas phase recombination and concentration layer gradient. The recombination loss is calculated from the theoretical relationship resulting from the processes

$$O + NO + O_2 \rightarrow NO_2 + O_2 \qquad \text{(III)}$$

$$O + O_2 + M \rightarrow O_3 + M \quad (M = O_2) \qquad \text{(II)}$$

It was assumed that the reaction time between detection points was too short to permit any significant contribution from

$$O + NO_2 \rightarrow O_2 + NO \qquad \text{(IV)}$$

and

$$O + O_3 \rightarrow O_2 + O_2 \qquad \text{(V)}$$

Any contribution from these reactions would simply increase the concavity of the curves. The concentration gradient in $\rho_{[O]}$ between the catalytic surface and the free stream was calculated from the Sherwood number, Sh obtained as described in detail in Section II. It will be seen that the general shape of the titration curves is similar to those in Figure 7.

Atom concentrations were determined for a number of different conditions as summarized in Table III.

Table III

RESULTS OF PROBE DETERMINATION OF $p_{[O]}$

RF at 700 volts

p_{tot} (mm Hg)	$F_{Ar+O_2} \times 10^4$ (mole sec^{-1})	u_∞ (cm sec^{-1})	$F_{NO_2} \times 10^6$ (mole sec^{-1})	$p_{[O]}$ (mm Hg)
4.35	5.43	488	8.0	0.0722
4.35	5.43	488	8.05	
5.73	5.40	367.5	6.63	0.0788
5.73	5.40	367.5	6.65	
5.73	5.84	397.5	7.5	0.0838
5.73	5.84	397.5	7.7	
4.73	5.40	445.0	7.5	0.0761
4.73	5.40	445.0	8.0	

2. Application of the Method to the Measurement of Atom Decay Rates

With the development of more sensitive probes, it became evident that the gauge technique offered an excellent means of measuring the rate of decay of atom concentrations as the pulse moved down the tube. Measurements were made, in separate experiments, of $\dot{q}$ resulting from identical pulses (there was no problem with reproducibility in this respect).

With a knowledge of the ratio of $\dot{q}_{upstream}/\dot{q}_{downstream}$ it was possible in principle to calculate the rate of atom decay. However, the only rate observations made were at a considerably earlier stage of the research than that at which the final γ measurements were made. Pure oxygen had been used as the flow gas* and a number of additional changes, which were eventually found necessary, had not been made. However, it was found that excellent reproducibility could be obtained. Thus, it would appear that this method should provide a rather clear-cut and accurate method of measuring various processes involving atom decay. It should be possible to extend this method to hydrogen and nitrogen atoms as well as to any other species which provide recombination heating on catalytic surfaces.

---

*See previous sections concerning spurious heating in O_2.

C. Conclusions

It has been shown that oxygen atom concentrations can be accurately determined in pulsed oxygen atom flows by combining the use of thin-film thermometry with the NO_2 titration technique. In addition, feasibility has been established for the use of these gauges in measuring homogeneous decay rates of oxygen atoms and probably other recombining atoms in pulsed flows.

IV. AN INTERPRETATION OF INITIAL RECOMBINATION HEATING IN TERMS OF THE RATE OF OXIDATION

In the first section of this report, we have described the measurement of the initial and rapid process whereby γ, the surface recombination efficiency, undergoes a complex time-history until a stable state is achieved. It has been possible to interpret the changes in recombination heat-transfer which are responsible for these changes in γ, in terms of the rate of oxidation of the metal by atomic oxygen. Instead of waiting for the slow gas-solid adsorption processes at high coverage, as is usually done, it is possible here to follow instantaneously the rapid interactions of atoms with the bare surface.

A. Experimental

The apparatus is that fully described in the previous sections. The gauges used were both of the stagnation and the circumferential type as indicated in the text and figures.

B. Discussion

It is important to note, in the ensuing discussion, that the heat evolution with which we are concerned is not that of direct chemisorption of the oxygen atoms on the metal surface. It is rather that evolved by a catalyzed recombination of the atoms on the surface into molecules which then leave the surface as a gas.* From previous work[1, 2] it has been shown that bare metals themselves are not, in general, very catalytic; that the ability of a metal to cause catalytic recombination is directly correlated with, and dependent on, oxide formation. Thus, if the recombination heating can be measured from the very inception of the metal-atomic gas interaction, the rate at, and extent to which the gaseous atom is interacting with the metal lattice can also be determined. In addition, it then becomes possible to deduce other fundamental characteristics of the atoms, metals and interactions involved.

---

*As discussed in Section II, it is quantitatively impossible to account for any significant fraction of the heat evolved, in terms of metal oxidation.

Examples of the types of $\dot{q}$ - t curves resulting from the interaction of atomic oxygen with a number of metals are shown in Figures 8a and 8b. Figure 8a represents data obtained by means of the circumferential gauge in the Ar-O_2 studies of Section II. The data of Figure 8b comprise initial observations made by means of a stagnation gauge using pure O_2. This was prior to the change to Ar-O_2 so that these latter data are subject to effects due to O_2^* and several other uncertainties subsequently eliminated. As has been noted previously, each surface yields its own characteristic trace on its initial exposure to atomic oxygen and can in fact be virtually identified by this "conditioning". It must be emphasized that this initial trace does not represent interaction of O atoms with a "clean" surface, but one "cleanly" covered with adsorbed O_2 only. For, under the conditions of the experiment, although the surface is outgassed in a vacuum of 10^{-6} mm Hg or less, it must be exposed to molecular oxygen (and argon) before the atom pulse impinges on it. In general, these traces can be interpreted in terms of an interaction of atomic oxygen with the metal, first to replace or "clean-up" the adsorbed O_2 with chemisorbed O atoms and in some cases to form an unstable oxide. After this initial step, the rate of heat transfer drops down and subsequently begins to rise again when the oxygen atoms actually begin to form chemical bonds in the metal lattice yielding a stable oxide at a rate, and with a catalytic recombination efficiency, characteristic of the metal as described in Section II. The curves of Figure 8 (all corrected for noncatalytic or thermal heat transfer by substracting out the $\dot{q}$ recorded simultaneously on a noncatalyst, TiO_2) have been interpreted in terms of the formation of an oxide as described above so that attainment of a peak value of $\dot{q}$ represents completion of the oxide formation that catalyzes the surface recombination, as previously mentioned. Rates have been extracted from the curves of Figure 8, by calculating the time required for $\dot{q}$ to rise from its low value to $1/e$ of the peak value ($\tau_{1/e}$) in accordance with the pattern indicated in the preceeding description. The reciprocal of $\tau_{1/e}$ is taken as representative of the rate of oxidation. The results are given in Table IV.

Table IV

RELAXATION TIMES FOR INITIAL METAL OXIDATION

Circumferential Gauge in 10% O_2 in Ar

Metal	P_{tot} (mm Hg)	$P_{[O]}$ (mm Hg)	u_{∞} (cm sec^{-1})	$\tau_{1/e}$ (msec)	$1/\tau_{1/e}$ ($msec^{-1}$)
Ag	5.73	0.0838	397.5	22	4.55
Cu	5.73	0.0838	397.5	90	1.11
Fe	5.66	0.0856	410.5	107	0.94
Ni	5.66	0.0856	410.5	108	0.926
Au	5.66	0.0856	410.5	220	0.45

Stagnation Gauge in 100% O_2

Metal	P_{tot} (mm Hg)	$P_{[O]}$ (mm Hg)	u_{∞} (cm sec^{-1})	$\tau_{1/e}$ (msec)	$1/\tau_{1/e}$ ($msec^{-1}$)
Ag	5.0	0.08	660	10.8	9.3
Cu	5.0	0.08	660	24.2	4.1
Fe	5.0	0.08	660	63.8	1.6
Ni	5.0	0.08	660	135.5	0.7

It is clearly seen that the rate at which the atoms penetrate and react with the metal lattice varies widely from several milliseconds for silver to hundreds of milliseconds for nickel. Furthermore there are differences in the catalytic ability of the compound formed and in the stability of the compounds.

With rates of the initial oxidation of the metal lattice deduced from these data, it is then in order to seek the fundamental property of a metal which determines its rate of oxidation. It is believed this has been found in terms of the strength of the metal-metal bond of the lattice which the O atom must rupture in order to enter the lattice structure. This bond strength in turn may be characterized by the heat of sublimation, ΔH_s , of the metal. If this is correct, then it should be possible to incorporate the ΔH_s into a bond energy and this in turn into an activation energy. Thus, using the Hirshfelder rule[17] for the sake of simplicity, the rate of incorporation of an oxygen atom into the metal lattice should be proportional to $e^{-E_{act}}$ $\cong e^{-0.06\Delta H_s}$. A plot of the rate terms $1/\tau_{1/e}$ of Table IV should, therefore, show a monotonic relationship between rate and activation energy. These plots are shown on Figure 9 for both sets of data.

It will be seen that, in general, the higher the heat of sublimation, the faster the reaction and that the relationship forms reasonably smooth curves except for the case of Au. It is also interesting to note that the order is the same for both curves in spite of the fact that the early stagnation data involve 100% O_2 and hence O_2^*, as well as other experimental imperfections, as indicated previously. One might conclude from this, that the ability to recombine atomic oxygen and to de-excite O_2^* are, more or less, in the same order although obviously these abilities do not bear any simple relationship to each other.

It would appear that this interpretation possesses sufficient merit to warrant more sophisticated studies of initial oxidation rates along these lines. The relevance to corrosion and erosion of metals is especially striking. Among the requirements for more sophisticated studies are more definitive surface preparation, characterization and outgassing (e.g., ultra-high vacuum) and the elimination of molecular oxygen from the scene of initial oxidation.

C. Conclusions

It has been demonstrated that the recombination heat-transfer studies of metals in pulsed flows of atomic oxygen may be interpreted in a manner which provides knowledge of the initial rates of oxidation of the metal. A relationship is shown to exist between the rate of oxidation and the metal's heat of sublimation.

V. PREVIOUS PUBLICATIONS AND REPORTS PRODUCED UNDER CONTRACTS AF 49(638)-782 AND AF 49(630)-1487

W. J. Rae, Catalytic Surface Recombination in Boundary Layer Profiles of the Falkner-Skan Type, CAL Report No. AF-1412-A-1, September 1962.

A. L. Myerson, Interim Report on Transient Heat-Transfer Measurements of Catalytic Recombination in a Step-function Flow of Atomic Oxygen, CAL Report No. AF-1412-A-2, August 1962.

Final Technical Progress Report on Catalytic Recombination in Step-function Flows of Atomic Oxygen, AFOSR Contract No. AF 49(638)-782, Cornell Aeronautical Laboratory, January 1965.

A. L. Myerson, Silver-Catalyzed Surface Recombination in a Step-function Flow of Atomic Oxygen, J. Chem. Phys. 38, 2043 (1963).

A. L. Myerson, Mechanisms of Surface Recombination from Step-function Flows of Atomic Oxygen over Noble Metals, J. Chem. Phys. 42, 3270 (1965).

J. O. Bohachevsky and D. F. DeSanto, A Method for Determining Catalytic Efficiency of Surfaces, CAL Report No. AI-2187-A-4, February 1967.

VI. REFERENCES

1. A. L. Myerson, J. Chem. Phys. 38, 2043 (1963)

2. A. L. Myerson, J. Chem. Phys. 42, 3270 (1965).

3. R. A. Hartunian, W. P. Thompson and S. Safron, J. Chem. Phys. 43, 4003 (1965).

4. W. A. Hardy and J. W. Linnett, Symp. Comb. 11, Berkeley, 1966, p. 167.

5. H. Wise and B. J. Wood, Advances in Atomic and Molecular Physics, Vol. 3, Academic Press, N. Y. (1968), pp. 291-348.

6. M. A. Clyne, D. J. McKenney and B. A. Thrush, Trans. Faraday Soc. 61, 2701 (1965).

7. I. O. Bohachevsky and D. F. DeSanto, A Method for Determining Catalytic Efficiency of Surfaces, CAL Rept. No. AI-2187-A-4, February 1967.

8. G. M. Prok, Effect of Surface Preparation and Gas Flow on Nitrogen Atom Surface Recombination, NASA Tech. Note D-1090 (1961).

9. R. Hilpert. Forsch. Ing. -Wes., 4215 (1933).

10. W. E. Ranz and W. R. Marshall, Jr., Chem. Eng. Progress 48, 141 and 173 (1952).

11. R. D. Brokaw, Alignment Charts for Transport Properties for Nonpolar Gases and Gas Mixtures at Low Density, NASA Tech. Rept. R-81 (1961).

12. S. Krongelb and M. W. P. Strandberg, J. Chem. Phys. 31, 1196 (1959).

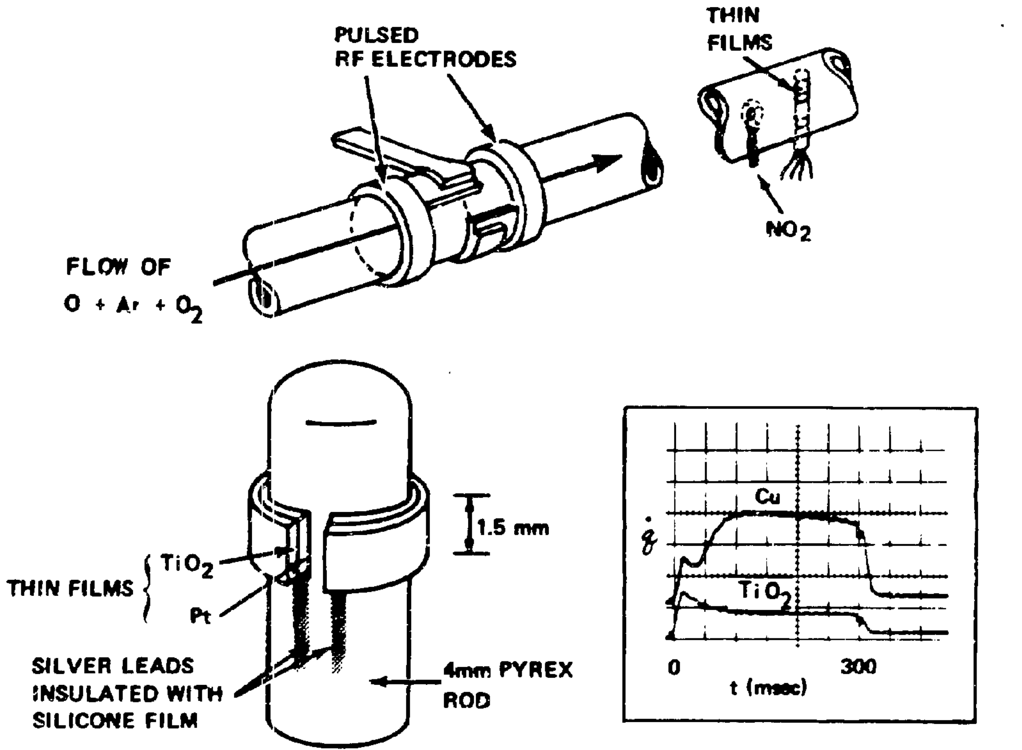
13. J. C. Greaves and J. W. Linnett, Trans. Faraday Soc. 54, 1323 (1958).

14. P. G. Dickens and M. B. Sutcliffe, Trans. Faraday Soc. 60, 1272 (1964).

15. L. Elias, E. A. Ogryzlo and H. I. Schiff, Canadian J. Chem. 37, 1680 (1959).

16. A. A. Westenberg and N. DeHaas, J. Chem. Phys. 40, 3087 (1964).

17. A. A. Frost and R. G. Pearson, Kinetics and Mechanism, Wiley, N. Y. (1953), p. 103.



SCOPE TRACE FROM COPPER FOIL

Figure 1 THIN-FILM RESISTANCE GAUGE AND FLOW SYSTEM

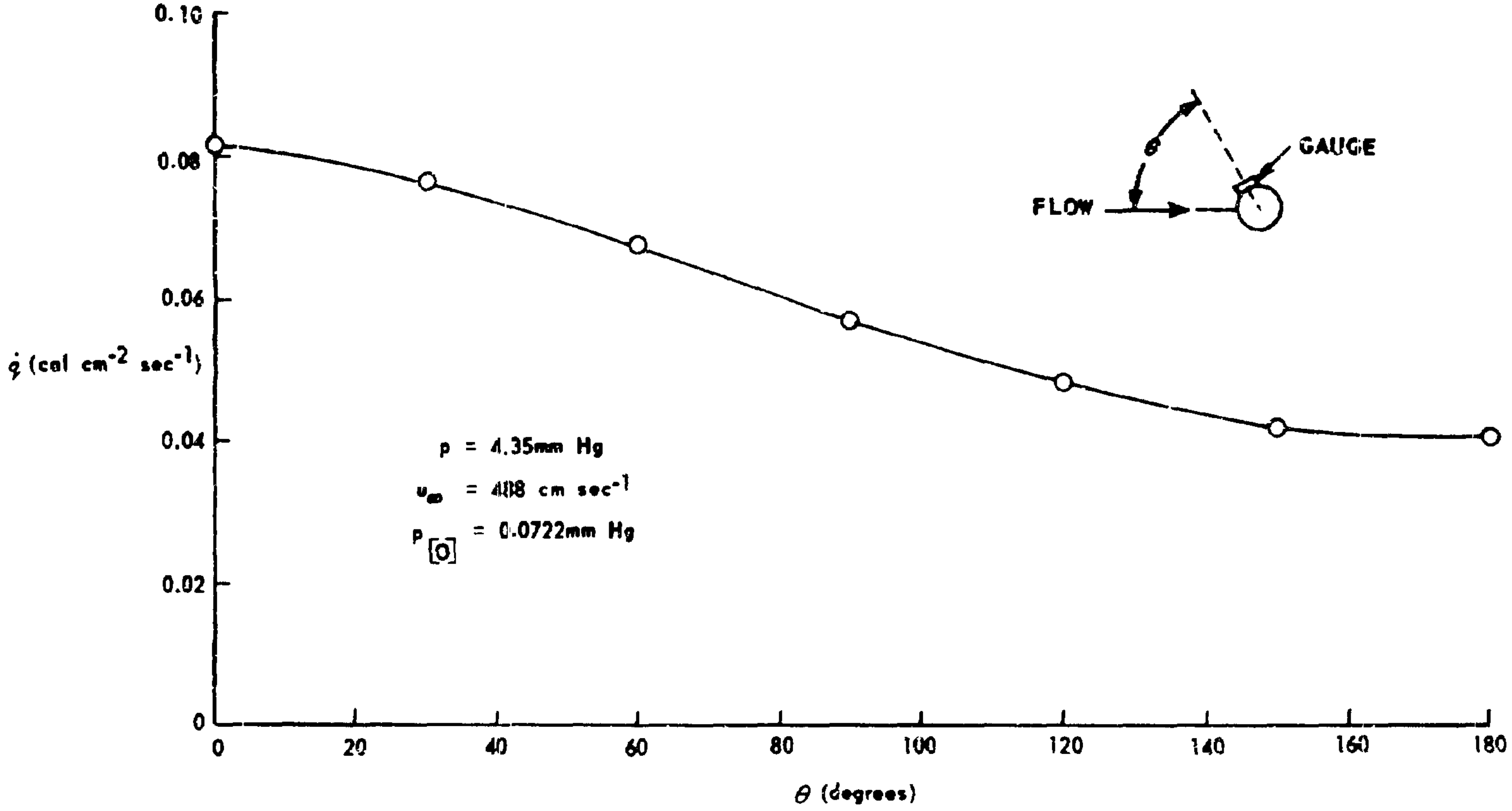
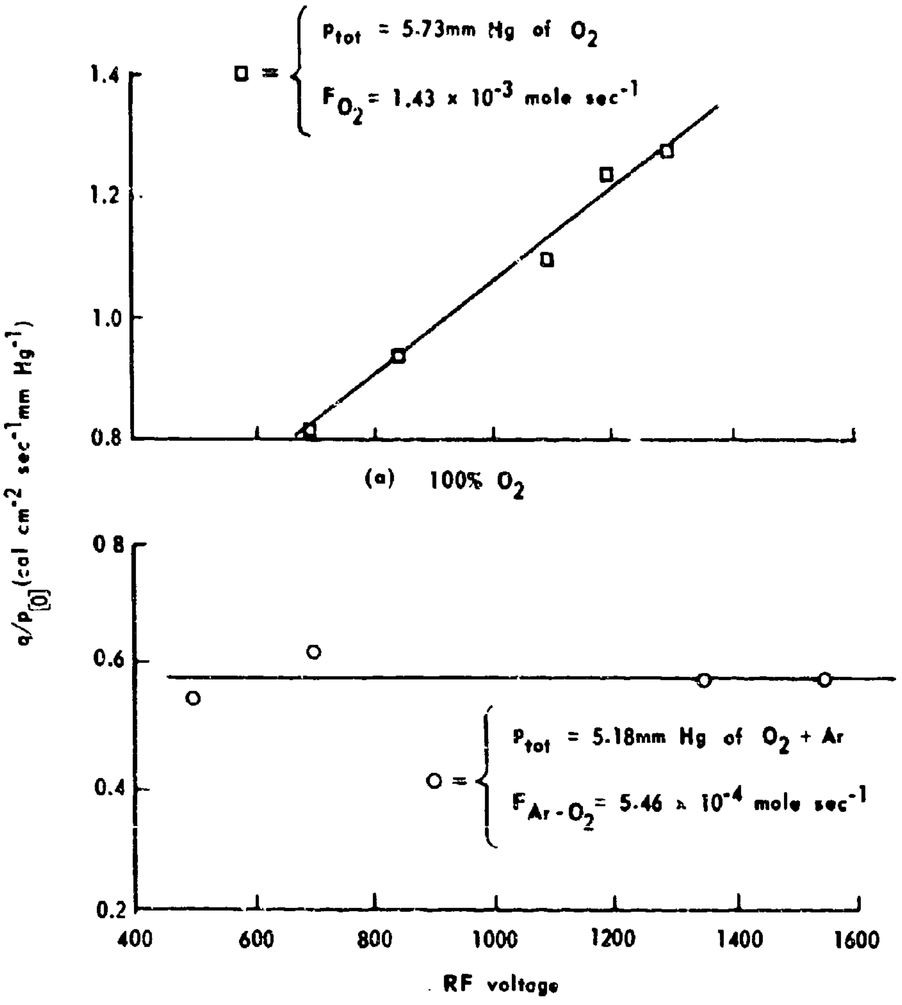


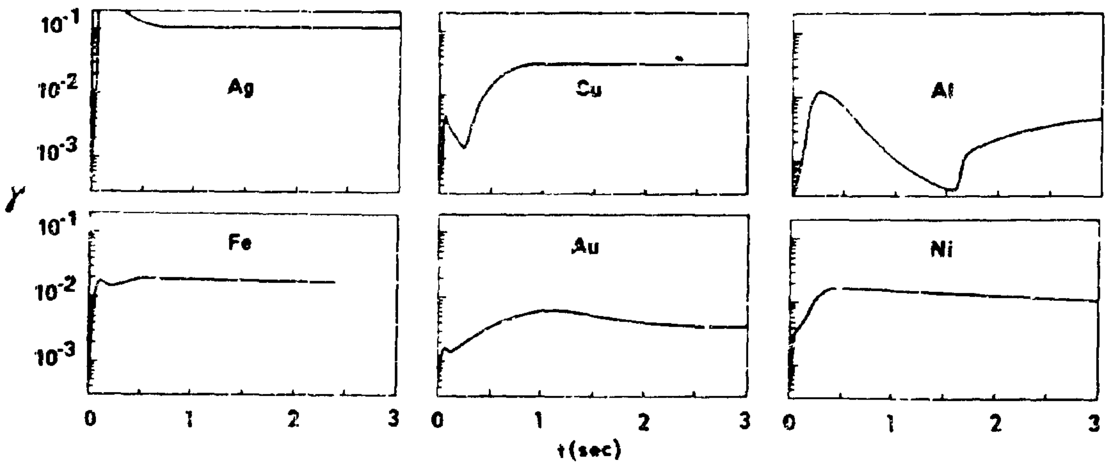
Figure 2 HEAT-TRANSFER TO A STAGNATION GAUGE AS A FUNCTION OF ITS ANGLE θ FROM THE DIRECTION OF FLOW



(a) 100% O_2

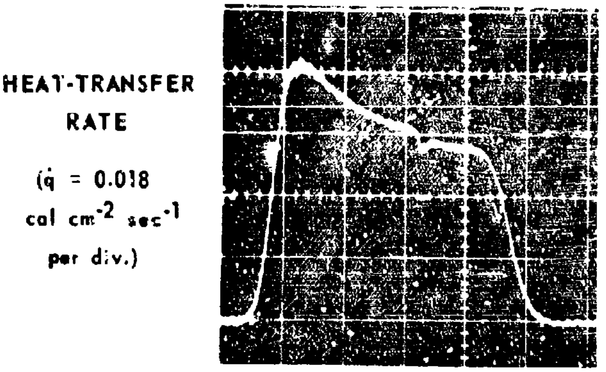
(b) 10% O_2 IN Ar

Figure 3 HEAT TRANSFER PER OXYGEN ATOM AS A FUNCTION OF RF ELECTRODE VOLTAGE

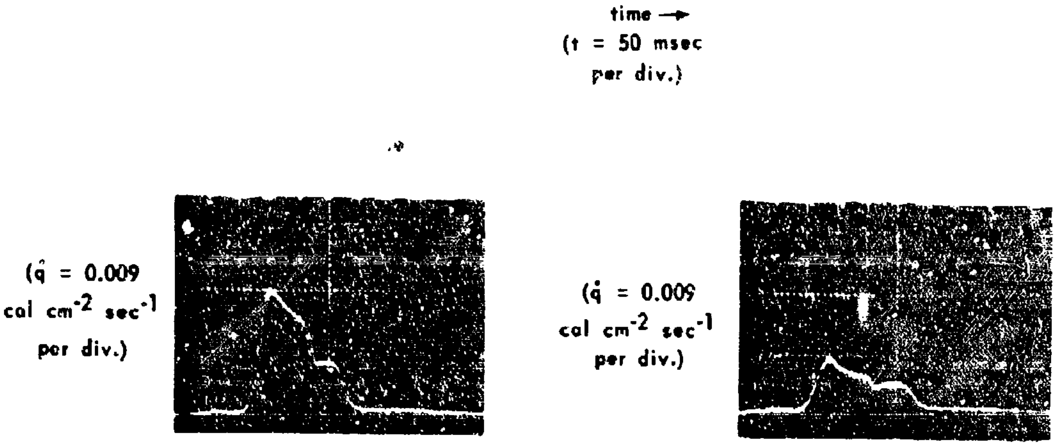


	$P_{[0]}$ (mm Hg)	P_{to}, (mm Hg)	u_{∞}(cm sec^{-1})
Ag,Cu	0.084	5.73	398
Al,Fe,Au,Ni	0.086	5.66	411

Figure 4 DEPENDENCE OF SURFACE RECOMBINATION EFFICIENCY (γ) ON EXPOSURE TO ATOMIC OXYGEN



STANDARD: NO NO_2 ADDED



PART OF O-ATOMS REMOVED BY NO_2

MOST OF O-ATOMS REMOVED BY NO_2

P_{tot} = 5.73mm Hg

F_{Ar+O_2} = 5.84 x 10^{-4} mole sec^{-1}

RF voltage = 700

Figure 5 STAGES IN THE DETERMINATION OF THE OXYGEN ATOM CONCENTRATION

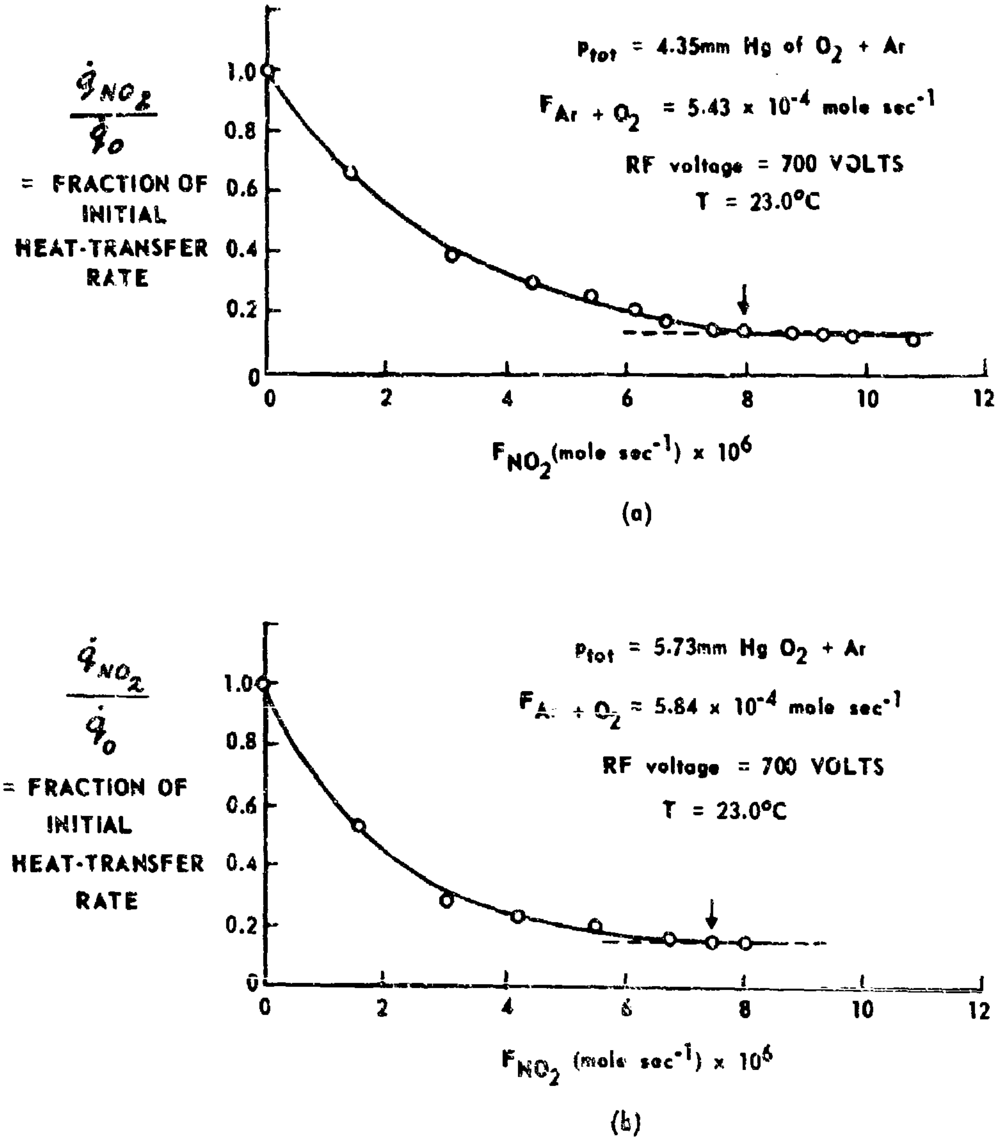


Figure 6 HEAT TRANSFER RATE AS A FUNCTION OF NO_2 ADDITION IN THE DETERMINATION OF [O]

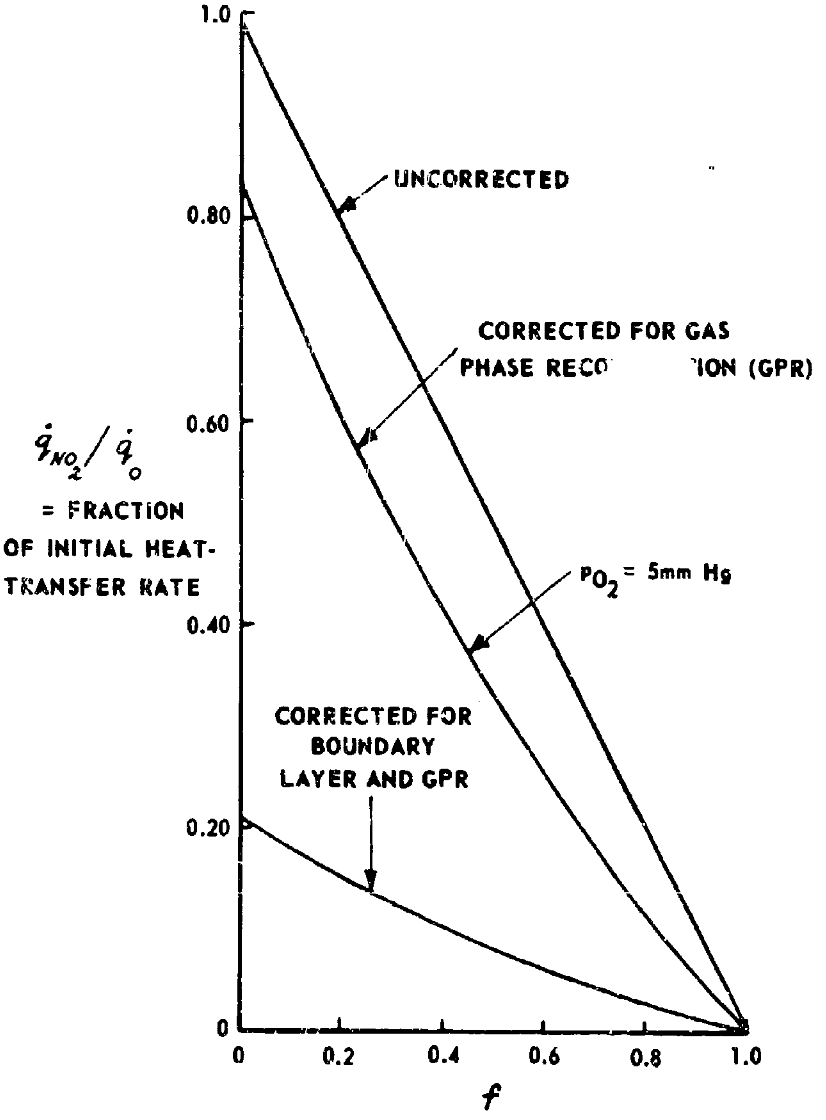
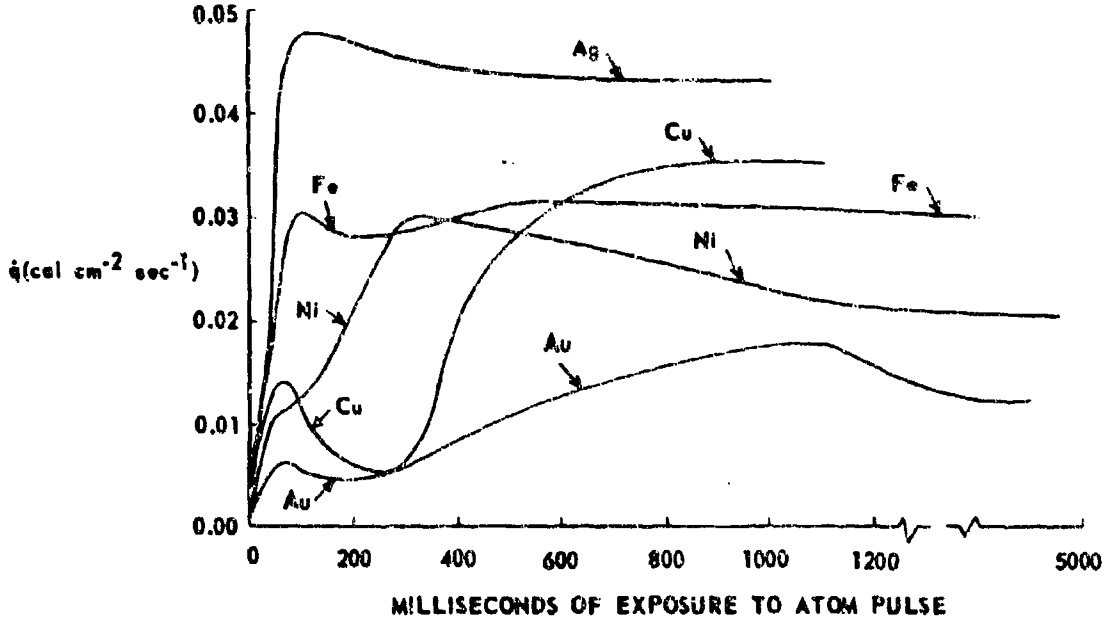
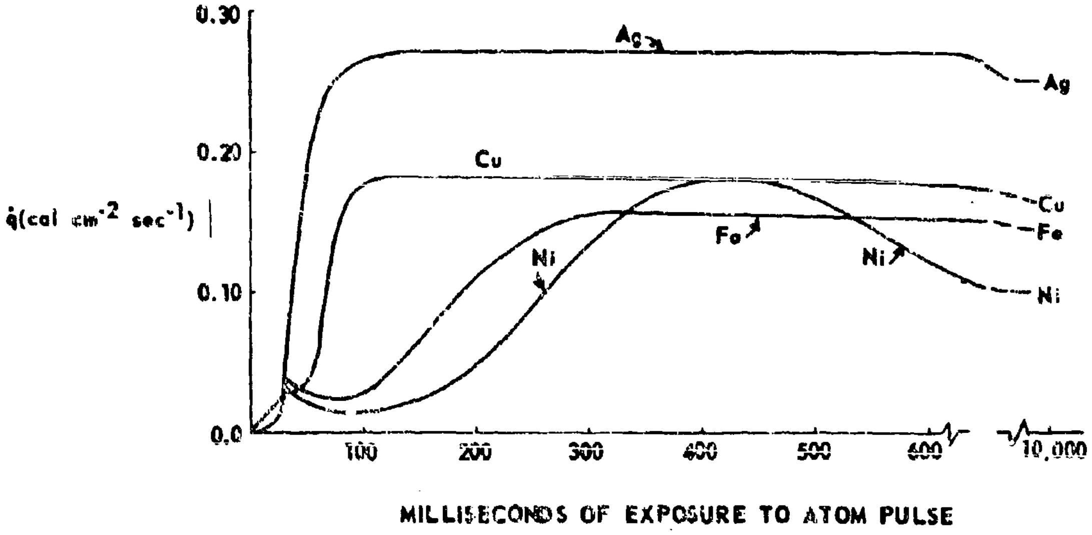


Figure 7 CALCULATED HEAT TRANSFER RATE AS A FUNCTION OF FRACTION (f) OF ATOMIC OXYGEN REMOVED BY NO_2



(a) FOR CIRCUMFERENTIAL GAUGE IN 10% O_2 IN Ar



(b) FOR STAGNATION GAUGE IN 100% O_2

Figure 8 RECOMBINATION HEAT TRANSFER DURING INITIAL INTERACTION OF METALS WITH OXYGEN ATOMS

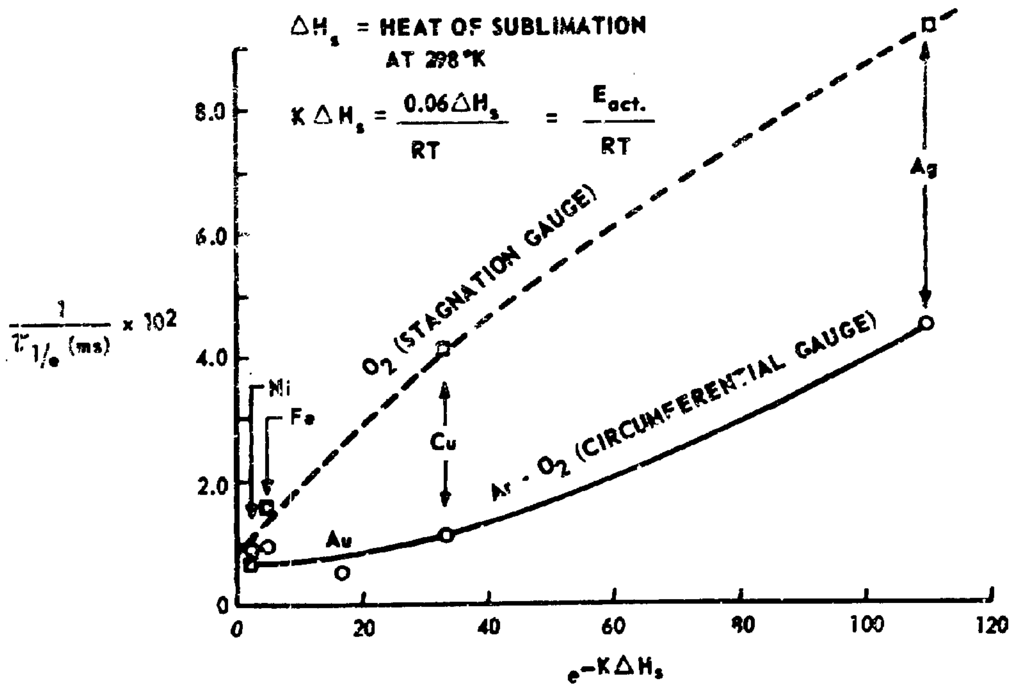


Figure 9 RATE OF INITIAL OXIDATION BY O ATOMS AS A FUNCTION OF THE METALLIC HEAT OF SUBLIMATION

APPENDIX A

The following table and figures are presented as an appendix because of their detail. Table A-I includes all the experimental and theoretical parameters involved in the final measurements which provided the results given in Table I and Figure 4 of the report. Figures A-1 and A-2 are detailed schematic diagrams of the complete apparatus used in the determination of γ for the various metals studied, and the very small flows of NO_2 used in the modified titration procedure for the determination of $[O]$.

Table A-1
COMPLETE DATA FOR TIME-RESOLVED γ DETERMINATIONS

Expt. No.	P_{tot} (mm Hg)	$P_{[O]}$ (mm Hg)	$\dot{q}$ (cal cm^{-2} sec^{-1})	Sh Sherwood Number	u_∞ (cm sec^{-1})	t (msec)	γ
Ag 1	5.73	0.0788	0.0398	1.87	367.5	STABLE-	0.101
Ag 2	4.35	0.0722	0.0477	1.90	488.0	STATE	0.108
Ag 3	4.73	0.0761	0.0456	1.90	445.0	↓	0.090
Ag 4	5.73	0.0838	0.0437	1.91	397.5		0.119
Ag 5	5.73	0.0838	0.0445	1.91	397.5		0.144
Ag 6	5.73	0.0788	0.0405	1.87	367.5		0.122
Ag 7	4.35	0.0722	0.0480	1.90	488.0		0.115
Ag 8	5.73	0.0788	0.0410	1.87	367.5		0.143
Ag 9	5.73	0.0838	0.0435	1.91	397.5		0.110
Ag 10	4.35	0.0722	0.0480	1.90	488.0		0.115
EAg 1	5.73	0.0838	0.0476	1.91	397.5	100	–
EAg 2	5.73	0.0838	0.0440	1.91	397.5	500	0.125
EAg 3	5.73	0.0838	0.0435	1.91	397.5	1000	0.110
Cu 1	5.73	0.0838	0.0144	1.91	397.5	70	0.0049
Cu 2	5.73	0.0838	0.0094	1.91	397.5	120	0.0028
Cu 3	5.73	0.0838	0.0056	1.91	397.5	270	0.0015
Cu 4	5.73	0.0838	0.0213	1.91	397.5	420	0.0092
Cu 5	5.73	0.0838	0.0351	1.91	397.5	820	0.031
Au 1	5.66	0.0856	0.0064	1.92	410.5	65	0.0017
Au 2	5.66	0.0856	0.0052	1.92	410.5	120	0.0014
Au 3	5.66	0.0856	0.0105	1.92	410.5	420	0.0031
Au 4	5.66	0.0856	0.0135	1.92	410.5	750	0.0043
Au 5	5.66	0.0856	0.0181	1.92	410.5	1100	0.0066
Au 6	5.66	0.0856	0.0143	1.92	410.5	1700	0.0047
Fe 1	5.66	0.0856	0.0306	1.92	410.5	90	0.0184
Fe 2	5.66	0.0856	0.0283	1.92	410.5	200	0.0153
Fe 3	5.66	0.0856	0.0318	1.92	410.5	500	0.0204
Fe 4	5.66	0.0856	0.0303	1.92	410.5	2400	0.0180
Ni 1	5.66	0.0856	0.0110	1.92	410.5	50	0.033
Ni 2	5.66	0.0856	0.0298	1.92	410.5	310	0.0172
Ni 3	5.66	0.0856	0.0210	1.92	410.5	4400	0.0085
Al 1	5.66	0.0856	0.0254	1.92	410.5	250	0.0121
Al 2	5.66	0.0856	0.0221	1.92	410.5	430	0.0093
Al 3	5.66	0.0856	0.0098	1.92	410.5	730	0.0029
Al 4	5.66	0.0856	0.0096	1.92	410.5		0.0028
Al 5	5.66	0.0856	0.0035	1.92	410.5		0.00088
Al 6	5.66	0.0856	0.0016	1.92	410.5	1600	0.00039
Al 7	5.66	0.0856	0.0048	1.92	410.5	1680	0.00125
Al 8	5.66	0.0856	0.0085	1.92	410.5	2050	0.0024
Al 9	5.66	0.0856	0.0147	1.92	410.5	3200	0.0049
Al 10	5.66	0.0856	0.0184	1.92	410.5	4800	0.0068

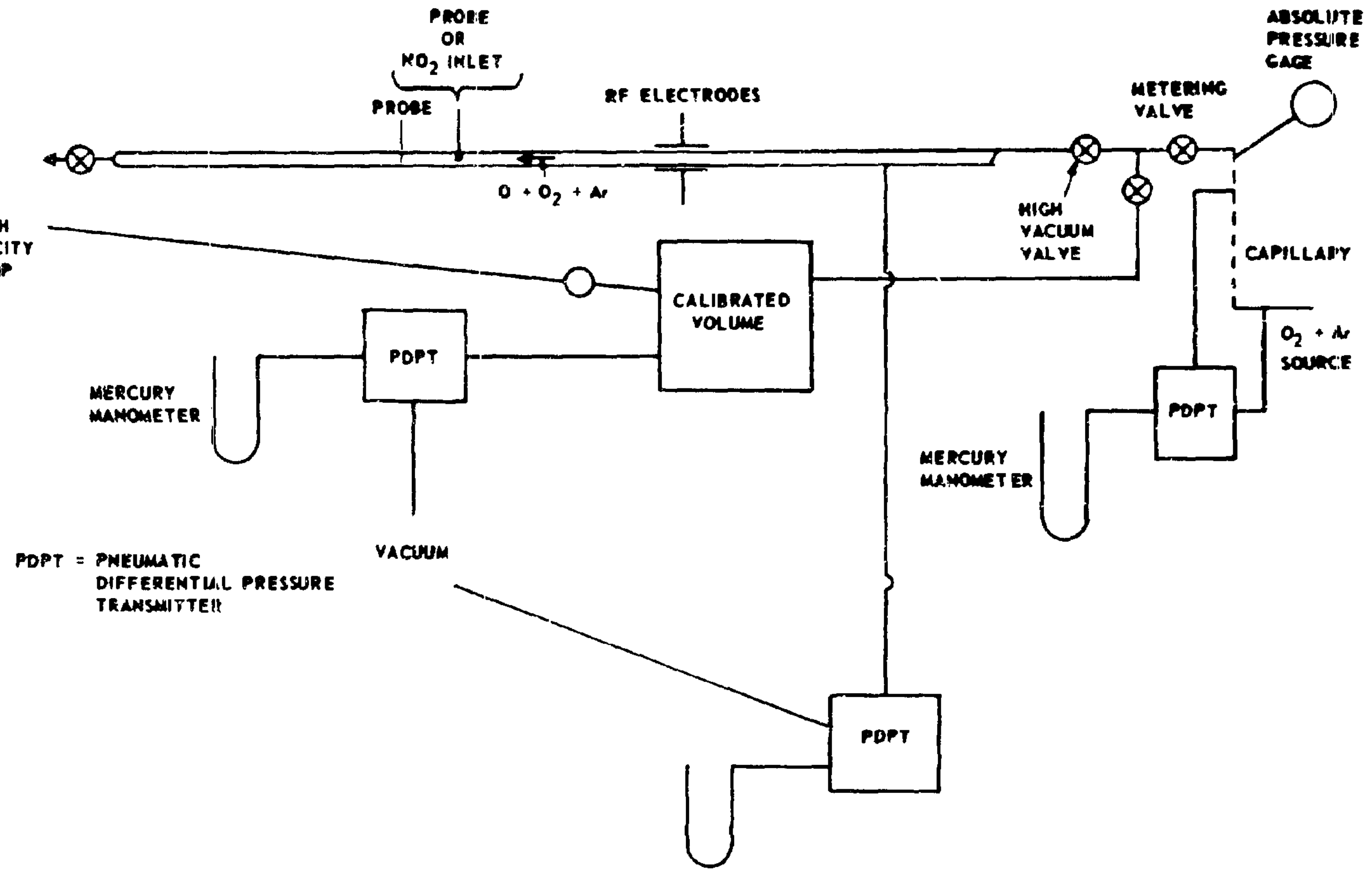
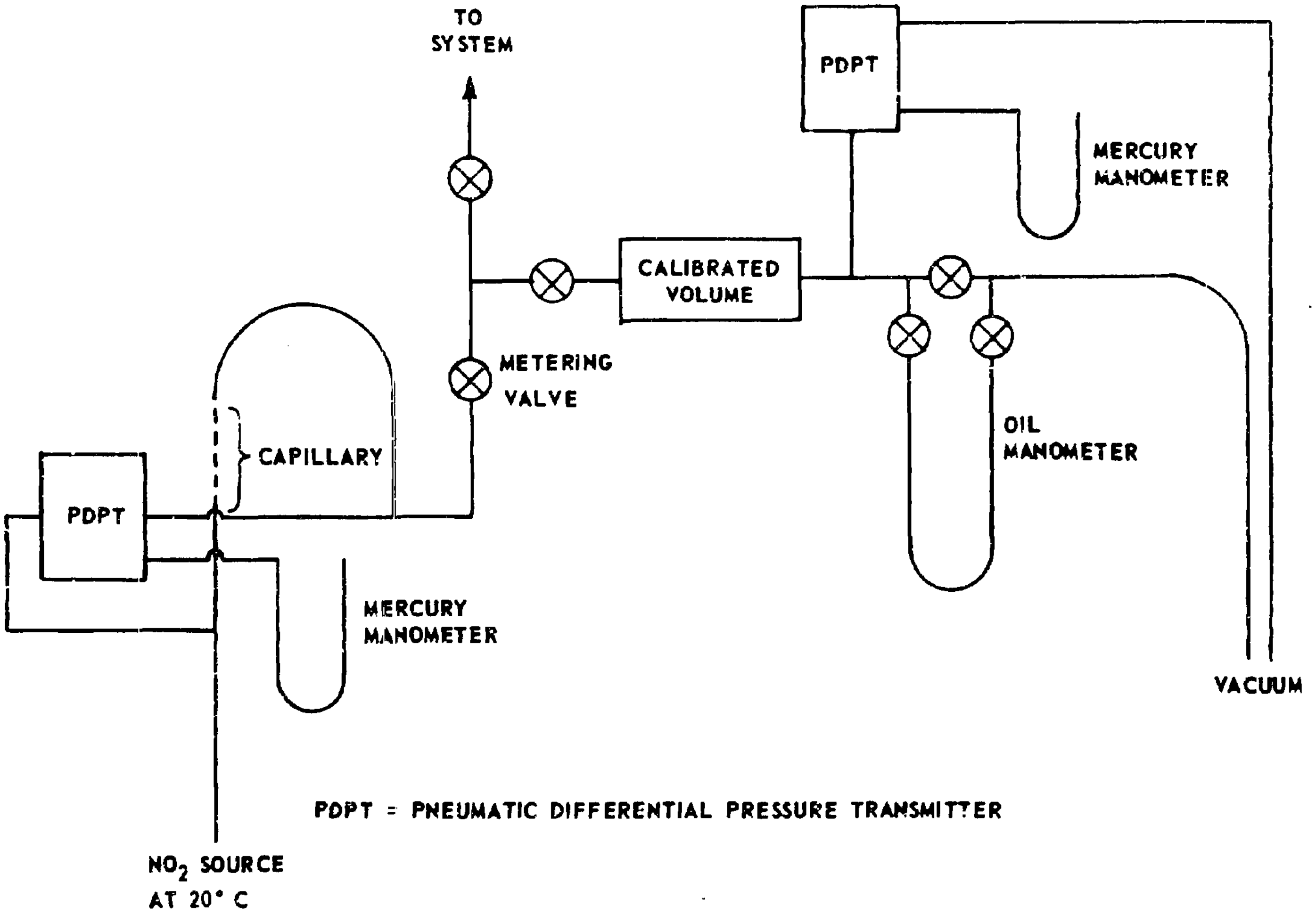


Figure A-1 DETAILED SCHEMATIC DIAGRAM OF PULSED OXYGEN ATOM FLOW SYSTEM



PDPT = PNEUMATIC DIFFERENTIAL PRESSURE TRANSMITTER

Figure A-2 DETAILED SCHEMATIC DIAGRAM OF APPARATUS FOR MEASUREMENT OF NO_2 FLOW RATES

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Cornell Aeronautical Laboratory, Inc.
Aerodynamic Research Department
Buffalo, New York 14221

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE
SURFACE RECOMBINATION EFFICIENCIES IN FLOWS CONTAINING STEP-FUNCTION INCREASES IN ATOMIC OXYGEN

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Scientific Final

5. AUTHOR(S) (First name, middle initial, last name)
Myerson, Albert L.

6. REPORT DATE
March 1968

7a. TOTAL NO. OF PAGES
43

7b. NO. OF REFS
17

8a. CONTRACT OR GRANT NO.
AF 49(638) 1487

b. PROJECT NO. 9783-01

c. 6144501F

d. 681307

9a. ORIGINATOR'S REPORT NUMBER(S)
CAL No. AF-2033-A-1

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
AFOSR-68-0893

10. DISTRIBUTION STATEMENT
1. This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES
TECH, OTHER

12. SPONSORING MILITARY ACTIVITY
AF Office of Scientific Research (SREM)
1400 Wilson Boulevard
Arlington, Virginia 22209

13. ABSTRACT

A study has been made of the initial interaction of atomic oxygen with various metals in steady flows which provide a step-function increase, or pulse, in the atom concentration. The observations have been made by means of thin-film resistance thermometry. The results are presented under three categories as follows:

Surface recombination efficiencies (γ) have been measured as a function of exposure time in pulses of oxygen atoms over various metals in Oseen flows. Cylindrical, circumferentially-coated, thin-film resistance thermometers were used to determine the rate of heat transfer. The relationship between the surface and free stream concentration of oxygen atoms was obtained by means of the mathematical analogy between heat and mass transfer. It was possible to use relatively high partial pressures of atomic oxygen and carrier gas (1% atomic oxygen in a flow pressure of 4 to 6 mm Hg of an Ar-O_2 mixture) which are important to the accuracy of the measurements of many of the parameters involved. Under these conditions, the dependence of γ on exposure time was obtained as a function of time for periods up to several seconds. Each of the metals investigated exhibits a markedly different time history of γ during the period of initial gas-solid interaction, and the γ of each metal eventually reaches a final but different stable-state value. The final values are 0.12, 0.03, 0.17, 0.0085, 0.007, and 0.005 for Ag, Cu, Fe, Ni, Al, and Au respectively, which values are generally lower than those previously reported. Reasons for these differences are presented.

DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

Atom concentrations have been measured in pulsed or step-function flows of atomic oxygen. This has been accomplished by employing thin-film heat transfer gauges along with the NO_2 titration technique, which normally makes use of a visual radiation end point. In the present work, the gauges have been used to detect the atoms remaining after various known fractions have been removed by NO_2. A curve results which can be extrapolated to obtain an accurate end point. A number of determinations made in this way are presented. In addition, it is shown how this technique can be applied to the determination of homogeneous atom decay rates.

The rate at which the recombination heat transfer on a newly exposed metal reaches its peak in a step-function flow of atomic oxygen has been interpreted in terms of the rate at which the catalytic oxide initially forms. The rates have been measured for two different series of heat transfer-time histories involving Ag, Cu, Fe, Ni, and Au. In addition, a relationship has been shown to exist between the rate of oxidation and the heat of sublimation of the metal.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
surface recombination efficiency						
oxygen atom-metal interactions						
step-function of atomic oxygen						
initial oxidation rates						
atom concentrations						
oxygen atoms						
exposure-dependent recombination						
recombination						
metal oxidation						