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KINETICS OF METAL ATOM OXIDATION REACTIONS

FINAL REPORT

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and JAMES J. HOUGHTON

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13. ABSTRACT

The tubular fast-flow reactor, previously used for reaction kinetic measurements at temperatures up to only 1000 K, has been adapted to reach temperatures up to 2000 K and has been applied to studies of gas phase reactions of metal atoms with O_2. The most extensive set of results obtained so far is for the Fe/O_2 reaction in an N_2 bath at 1600 K. This reaction proceeds via $Fe + O_2 \rightarrow FeO + O$ with a rate coefficient of $(3.6 \pm 1.4) \times 10^{-13}$ ml molecule^{-1} sec^{-1}. Extrapolation of the results suggests that $k(T) = 2.0 \times 10^{-10} \exp(-20,000/RT)$ ml molecule^{-1} sec^{-1}. Evidence has also been obtained at 1600 K for a wall oxidation reaction for which $\gamma_{Fe, 1600 K} \geq 10^{-1}$. Preliminary results for the Al reaction with O_2 at 1700 K are discussed. The experimental technique described here allows measurements to be made under reaction conditions overlapping those used in flame and shock-tube studies.

A design study for a wall-less reactor which would allow extension of metal atom oxidation studies down to about 200 to 300 K is also reported.

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REPORT SUMMARY

The Ivy Owl program requires knowledge of the rate coefficients of the Fe/O_2 and Al/O_2 reactions and their temperature dependence. Since no conventional experimental technique appears capable of providing such data, a novel apparatus (already at the initiation of this work partially developed under other sponsorship) was completed and adapted to the study of Fe and Al reaction kinetics. This tubular high temperature fast-flow reactor has been used for the measurement of the rate coefficient of the Fe/O_2 reaction at 1600 K. Preliminary, as yet inconclusive, information on the Al/O_2 reaction at 1700 K has also been obtained. The apparatus also appears uniquely suited to the study of the kinetics of free metal atom reactions of importance to DoD problems other than those of Ivy Owl. Design studies for a wall-less reactor have been made to allow future studies of oxidation by thermally unstable species (viz. O_3), the extension of the Fe/O_2 and Al/O_2 work to temperatures below ≈ 1200 K and inclusion of U-atom reactions.

The reactor is described in detail in Appendix A. Very briefly, it consists of a 2.5 cm i.d., alumina tube contained in a 25 cm i.d. 95 cm long vacuum chamber; the reactor is heated using Pt-40% Rh resistance wire. With this reactor the useful working range of the fast-flow reactor technique, previously limited to the 200 - 1000 K range, has been extended to 2000 K, allowing studies of the kinetics of refractory species such as Fe and Al. Moreover, since the reaction conditions obtainable with this reactor overlap those of flames and shock-tubes, a bridge is provided between low and high temperature kinetic methods.

The method for obtaining and reducing the data is discussed in Appendix B (and in a more concise form in Appendix C). The metal is vaporized inside the reactor and entrained in an inert carrier gas stream. Relative metal atom concentrations are measured via optical absorption at a port situated near the downstream end of the reactor. O_2 is introduced, through an axially movable nozzle, into the gas stream at concentrations several orders of magnitude larger than that of the metal atoms. Rate coefficients are obtained from the observed variation in relative metal atom concentration as a function of reaction time (proportional to distance along the reactor axis), O_2 concentration, total pressure and temperature.

The gas phase Fe/O_2 reaction at 1600 K in an N_2 bath at 15 to 60 Torr has been determined to be

$$Fe + O_2 \rightarrow FeO + O \tag{1}$$

with a rate coefficient $k_1 = (3.6 \pm 1.4) \times 10^{-13}$ ml molecule^{-1} sec^{-1}. Evidence

for heterogeneous oxidation of Fe in the presence of O_2 has also been obtained; the lower limit for the probability of Fe oxidation per collision with the reactor wall, γ, is found to be $\geq 10^{-1}$. While the temperature dependence of k_1 should be determined experimentally in our follow-up studies, we have for the present assumed the activation energy to be equal to the estimated endothermicity of Reaction (1), 20 kcal mole^{-1}. The above result then corresponds to $k_1(T) = 2.0 \times 10^{-10} \exp(-20,000/RT)$. This pre-exponential factor is within a factor of 2 to 3 of the gas kinetic collision frequency rate factor, which makes it unlikely that the activation energy can be appreciably greater than 20 kcal mole^{-1}. This value of $k_1(T)$ is consistent with published limit determinations obtained in shock tube and flame studies. For details of the Fe/O_2 study see Appendices B and C.

The Al/O_2 system in the 1 - 10 Torr range in an Ar bath at 1700 K has been studied next. Experimental problems of vaporizing the Al and obtaining reproducible measurements have now been resolved. However, the first series of experiments yielded apparent rate coefficients (on the order of 10^{-10} ml molecule sec^{-1}) which increased with decreasing pressure. Possible causes for these anomalous results are discussed in Section II of the body of the report. It is anticipated that more extensive experiments including measurements at both higher pressures and lower temperatures will help clarify the situation.

Two major candidate reactions for which the rate coefficients need to be known in the Ivy Owl program are the Al/O_3 and Fe/O_3 reactions. However, temperatures below about 500 K will have to be used in these studies, since thermal decomposition of O_3 is quite rapid at higher temperatures. A modification of the present reactor, viz. the "wall-less" flow reactor, appears suitable for studying refractory metal atom oxidation reactions at these lower temperatures. Our design for such a system is discussed in Section III of the report. It comprises, on the upstream end, a vacuum furnace/vaporizer unit similar to our present apparatus. Metal atom-containing gases from the vaporizer are to be expanded through a converging-diverging nozzle into a test section where O_3 is to be added. The nozzle and test section are similar to those used in some of our previous studies and will allow us to obtain well-defined supersonic jets with velocities up to Mach 3. Besides achieving the necessary temperature reduction, the use of supersonic jets is desirable since the O_3 reactions are likely to be fast. The jets readily maintain their identity over a sufficient flow distance to allow making the kinetic measurements necessary for very fast reactions (on the order of the collision rate.) The wall-less reactor would be suitable for temperatures in approximately the 200 to 1300 K range and hence would also allow extension of the Al/O_2 and Fe/O_2 studies to temperatures below 1000 K. Moreover, coupled with a suitable vaporizer, it would allow study of metals even less volatile than Fe and Al, such as U. Finally, for systems where major interference of wall reactions is encountered (Al/O_2 may be an example), the wall-less reactor appears to represent a preferred mode for obtaining kinetic data.

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I. INTRODUCTION

The goal of the present work is to measure rate coefficients for the reactions of gaseous Fe and Al with O_2 required for various Department of Defense applications.

The measurements are made with a heated cylindrical fast-flow reactor apparatus suitable for study of the kinetics of gaseous species at temperatures up to ≈ 2000 K. Rate coefficients are obtained from the observed variations in the relative metal atom concentration as a function of reaction time, O_2 concentration, and total pressure. The flow reactor is a high purity alumina cylindrical tube situated inside a vacuum furnace. The reactor and vacuum jacket have ports for optical observations. The metal is vaporized and entrained in an inert carrier gas stream. The O_2 is introduced into this gas stream at concentrations several orders of magnitude larger than that of the metal atoms. The basic measurement of the relative metal atom concentration as a function of reaction time is made via optical absorption of the requisite metal atom radiation emitted by a hollow-cathode lamp.

The major results of this study have been discussed in three publications (Appendices A - C of the present report) and concern the unique apparatus constructed for the measurements (Appendix A), the method for obtaining and reducing the data (Appendix B) and the results of the Fe/O_2 rate coefficient study at 1600 K (Appendices B and C). These results are not repeated in the body of the report, in which are discussed the preliminary findings on the Al/O_2 system and the results of a design study for a wall-less reactor. The latter would allow extension of the studies down to ≈ 200 K and the inclusion of O_3 and U as reactants.

II. Al/O_2 KINETICS

A. Experimental

1. Apparatus

In the course of these studies a major apparatus improvement was put into effect. The reaction tube now is a grooved alumina tube which holds the heating elements directly, thus bringing the heat source closer to the gas flow. The original muffle tube (see Fig. 2 of Appendix A) now serves as an extra heat shield. About 40% less of the 0.127 diam Pt-40% Rh resistance wire is required with this more efficient design, which also drastically reduces the power consumption (e.g., the power required to maintain the reactant gases at 1700 K is one-third of that previously required).

Since the reactor has now been in nearly continuous use for more than a year, some idea can be obtained of the lifetime of the various internal parts. The ceramic heat shields appear to have an indefinite lifetime (no failure encountered). The reactor (muffle tube) is subject to failure whenever a burn-out of the Pt/Rh heating wire occurs or metal spills from the vaporizer. In addition radial cracks develop at the observation port which lead to fractures when the apparatus is dismantled for any reason, such as a burn-out of the heating element.

2. Procedures and Preliminary Observations

The method followed for introduction of Al was arrived at after lengthy trial and error procedures. Al is supplied from a 4 cm deep, wide-lipped boron nitride crucible, which is preheated at ≈ 1100 K in a bell-jar under vacuum prior to filling with Al and introducing into the flow reactor. Ar is used as the bath gas; O_2 is introduced using the same Pt ring distributor as was used in the Fe/O_2 work. To prevent any systematic errors due to the specific Al concentrations used or deviations from the Lambert-Beer law, two Al absorption lines of different oscillator strengths are used; the 309.3 nm (gf = 0.79)[1] and the 394.4 nm (gf = 0.15)[1] lines.

Until the final five weeks of the contract N_2 was used as the bath gas (as in the Fe/O_2 studies). This caused a series of problems. The molten Al tended to bubble and creep over the edge of the baskets, resulting in a loss of Al-absorption signal and several broken reaction tubes. This problem was solved by using high purity Al wire (or shot) and melting the Al in a mock-up facility under one atmosphere of N_2. We then reduced the N_2 pressure slowly to 1 Torr and kept the molten Al under vacuum till bubbling ceased. The same problem does not arise when Ar is used as the bath gas. With Ar merely preheating the empty crucibles under vacuum suffices. The boron nitride crucibles themselves also deteriorated slowly in the presence of N_2 but not in Ar. Heavy deposits, which may interfere with the measurements, formed on the O_2 distributor ring in the presence of N_2. When Ar is used only a slight white deposit forms.

The preliminary Al/O_2 experiments in N_2 were made at temperatures from 1200 - 1700 K. To obtain sufficient Al vapor, the Al-containing crucibles were (at reactor temperatures below 1700 K) heated independently by surrounding them with tungsten resistance wire, the same procedure as followed in the Na experiments under the Sandia contract (cf. Section I. C. 2. of Appendix A). While the now resolved Al-creep problem prevented extensive experiments below 1700 K (by shorting out the tungsten wire), enough data were obtained to demonstrate that adequate Al concentrations were available to allow kinetic measurements to be made at temperatures at least as low as 1200 K.

To ascertain that no O_2-independent Al removal processes occur, blank experiments were performed for both N_2 and Ar bath gas. In these experiments the O_2 nozzle was traversed over the useful length of the reactor under the following three conditions: (i) no gas flowing through the nozzle, (ii) N_2 flowing through the nozzle, and (iii) Ar flowing through the nozzle. The rates of these N_2 and Ar nozzle flows used included the equivalent of the highest O_2 flow rate used. No evidence for Al consumption was found in any of these experiments.

B. Results and Discussion

All results obtained thus far pertain to a temperature of 1700 K. Figure 1 shows a typical individual run ($[Al]_{relative}$ versus reaction time) from which is obtained the pseudo-first order rate coefficient, k_{ps_1}, for Al consumption at fixed $[O_2]$, pressure and average gas velocity. A series of such runs in which $[O_2]$ is varied at constant pressure and average gas velocity yields the rate coefficient for the reaction

$$Al + O_2 \rightarrow AlO + O \qquad (2)^{\dagger}$$

under these conditions. A representative series is shown in Fig. 2. If the rate coefficient obtained is truly that for the homogeneous reaction (2) it should be independent of variation in pressure and temperature (as observed in the Fe/O_2 reaction, see the table in Appendices B or C). It may be seen from Table I

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† Reaction (2) is approximately thermoneutral, i.e. the bond dissociation energy of Al–O is approximately[2,3] equal to that of O_2, 5.1 eV.

TABLE I. APPARENT RATE COEFFICIENTS OF Al + $O_2 \rightarrow$ AlO + O IN Ar AT 1700 K

λ (nm)	P (Torr)	v ($m\ sec^{-1}$)	$[O_2]$ ($10^{13}\ ml^{-1}$)	[M] ($10^{16}\ ml^{-1}$)	$\bar{T}$ (K)	k (10^{-11} ml molecule^{-1} sec^{-1})
309.3	10	104	1.8 -11.5	5.6	1712	6.2
394.4	10	105	2.7 -11.5	5.6	1713	6.3
309.3	5.0	105	0.92- 5.5	2.8	1718	10.4
309.3	5.0	51	0.96- 4.6	2.8	1682	9.1
394.4	5.0	107	1.3 - 5.5	2.8	1724	10.0
309.3	2.5	54.5	2.7 - 8.8	1.4	1715	7.8
309.3	2.5	52.6	1.8 - 5.5	1.4	1698	10.7
394.4	1.0	108	0.9 - 4.3	0.56	1713	25.2

that the results obtained thus far, while apparently independent of flow velocity or absorption line used, show an increase in the apparent rate coefficient with decreasing pressure. The cause of this phenomenon is uncertain at the present time, but several possibilities should be considered.†

We will first examine the possibility that the Al-consumption observed is actually due to wall reactions and that a homogeneous rate coefficient could be obtained only if wall reactions can be suppressed. Analogy to the Fe/O_2 system, which was dominated at pressures near 3 Torr by a zero order (in $[O_2]$) wall reaction, but for which good data on the gas-phase reaction were obtained in the 15 to 60 Torr regime, suggests (i) that wall reactions could be important in the Al/O_2 system and (ii) that an extension of the experiments to higher pressures should be undertaken. However, if the trend in the Al/O_2 data is due to a wall reaction, then it must be a wall reaction of first order in $[O_2]$. Non-zero order wall reactions are less common but nevertheless quite possible; furthermore, changes in the order dependence of wall reactions are not an unusual phenomenon (see e.g. Ref. 4). A non-zero order wall reaction might result from the fact that at 1700 K equilibrium O_2 dissociation is on the order of 10%; while collisional homogeneous dissociation is far too slow ($k \approx 10^{-22}$ ml molecule^{-1} sec^{-1} for M = N_2, Ar, O_2)[5,6] to attain even a small fraction of this equilibrium value for O_2 dissociation at the reaction times involved (in our work 10^{-2} to 10^{-3} sec), wall dissociation could be rapid[7] and the reactive O-atom population absorbed on the vessel walls could then be directily proportional to

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† Table I contains the results obtained in the last month of the technical effort. Further work is currently in progress

$[O_2]$. While homogeneous oxidation of atomic Al by atomic O is necessarily a three-body process and hence slow, the wall-stabilized Al/O reaction could well be fast. One way in which we should further investigate this point involves studying the reaction at lower temperatures.

The following more quantitative analysis of the data (based on the data reduction procedures for heterogeneous oxidation of metal atoms outlined on p. 18 of Appendix B) argues rather *against* the possibility that our measurements pertain to a heterogeneous reaction over the full 1 - 10 Torr range. Evidence for the occurrence of a zero-order (wall) reaction can be obtained from the present data. As in the Fe studies, this process is indicated by the finite ordinate intercept† on all k_{ps_1} versus $[O_2]$ plots. The k_{ps_1} intercept from Fig. 2 of $\approx 0.5 \times 10^3$ sec^{-1} at 10 Torr would correspond to a probability of oxidation per Al-atom collision with the wall, γ, of $\approx 1 \times 10^{-2}$. The highest k_{ps_1} values measured thus far in the Ar work are about 10×10^3 sec^{-1}, cf. Fig. 2. At 10 Torr this would correspond to γ 2×10^{-1} if heterogeneous kinetics dominates. However, estimating[8] D_{Al-Ar} at 10 Torr and 1700 K as 0.6×10^3 cm^2 sec^{-1}, the diffusion controlled rate for k_{wall} would be $\approx 2 \times 10^3$ sec^{-1}. This suggests that the observed k_{ps_1} values, at least at 5 and 10 Torr, are too fast to be interpreted as due only to a wall oxidation process. Although mixing in our experimental configuration might be faster than calculated on the basis of a pure diffusional process, this observation certainly suggests that the above wall reaction hypothesis should be viewed with suspicion.

We have also considered changes in mixing rates as a second (but a priori unlikely) possible cause of the observed increase in rate coefficient with decreasing pressure. A ceramic bar was installed just downstream from the Al basket in a few experiments, but was found to not influence results. Similarly, a Pt grid installed just upstream from the O_2 nozzle had no apparent effect. Hence incomplete mixing does not seem to be the cause of the problem.

The third and probably most reasonable explanation of our data is that the homogeneous reaction has indeed a rate coefficient on the order of 10^{-10}ml molecule^{-1} sec^{-1}, i.e. within an order of magnitude of the gas kinetic collision frequency rate factor, and that the apparatus in its present form cannot be used to accurately measure such very fast reactions at 1700 K. An indication of such a difficulty is supplied by another peculiarity observed in the Al/O_2

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† In the earlier Al experiments in which N_2 was used as the bath gas, instead of Ar, generally much larger intercepts were obtained (up to about 5×10^3 sec^{-1}). This in fact constituted the main difference between the Ar and N_2 series. The latter, which were all obtained at 10 Torr, showed a great deal of scatter but within the accuracy of the data gave the same apparent first order rate coefficient.

experiments: the straight portion of the $[Al]_{rel}$ versus reaction time (distance) plots, Fig. 1, from which the k_{ps_1} data are obtained, terminates quite far upstream from the observation port. In fact most Al consumption occurs in the upstream useful half of the reactor (10 - 20 cm upstream from the observation port), cf. Fig. 1. In the Fe and Na experiments (Figs. 3 and 4 of Appendix A) this straight portion began, as anticipated, almost immediately downstream from the observation port. (At the observation port itself no useful measurements can be made due to the disturbance caused by the sweeper gas and the decrease in temperature.) Whether this observation has any bearing on the trend in the rate coefficients of Table I is not clear, but it is quite possible. It should be noted that, as a result of the fast rate, the O_2 concentrations used in the Al work are some two orders of magnitude lower than those used in the Fe work (the amount of O_2 needed to consume the metal atoms in a given reaction time is, for a reaction of first order in $[O_2]$, inversely proportional to the rate coefficient). This use of such low O_2 concentrations could cause a breakdown of our basic assumption (cf. Appendix B, page 9 or Appendix C, page 509) that $[Al] \ll [O_2]$. It may be possible to use lower $[Al]$ in future work if we would determine $[Al]_{rel}$ by resonance fluorescence rather than by absorption. This would require the optical measurements to be made at a 90° angle from the illumination port; such a modification of our apparatus does not appear to be very difficult to make and would enhance its versatility.

C. Conclusions

The first series of runs on the Al/O_2 reaction has led to ambiguous results. In view of the high quality data obtained in the Fe/O_2 experiments, this result is unexpected and disappointing. The problem will be analyzed further both theoretically and experimentally. The proper way to proceed with the experiments appears to be initially to use higher pressures and lower temperatures. The use of the reactor in a resonance fluorescence (rather than absorption) mode also is under active consideration. If such experiments fail to yield proper data on the Al/O_2 system it would be best to continue the study of this system in the planned supersonic jet wall-less reactor facility to be discussed in Section III. This facility is designed to study metal atom oxidation reactions at lower temperatures where O_3 can be used as a reactant (< 500 K). However, its use might also be required for very fast reactions and would definitely be indicated for reaction systems in which wall reactions prevent the measurement of homogeneous rate coefficients.

III. PLANNED WALL-LESS REACTOR FACILITY

Two major candidate reactions for which the rate coefficients need to be known in the Ivy Owl program are the Al/O_3 and Fe/O_3 reactions. However, to study O_3 reactions, temperatures not exceeding about 500 K will have to be used, as the thermal decomposition kinetics of O_3 are quite rapid at higher temperatures.[9] A modification of the present reactor, viz. the "wall-less" flow reactor, appears suitable for studying metal-atom oxidation processes at these lower temperatures. The ability to work at lower temperatures is also of importance to the Ivy Owl program for the study of O_2 reactions, for which extrapolations of rate coefficients down to ≈ 200 K are desired. Finally, and, in view of the findings on the Al/O_2 system (Section II) quite importantly, the wall-less reactor would facilitate the study of very fast reactions and would allow study of homogeneous kinetics free of the interference of wall reactions.

A. Design Considerations

An initial design for a wall-less reactor has been prepared during the course of the present study and is shown schematically in Fig. 3. It comprises, on the upstream end, a vacuum furnace/metal vaporizer similar to our present apparatus (Appendix A). The metal atom-containing gases from the vaporizer are now to be expanded through a converging-diverging nozzle into a supersonic flow reactor section where O_3 or O_2 is to be added. The nozzle and test section are similar to those used in some of our previous studies[10-11] of kinetics in supersonic flows and would allow us to obtain well-defined jets with velocities up to Mach 3. The use of supersonic jets appears desirable since the O_3 reactions are likely to be fast; these jets readily maintain their identity over a sufficient flow distance (i.e. ≈ 10 to 15 nozzle exit diameters)[12] to provide a reaction time scale of appropriate duration (10^{-4} to 10^{-3} sec) and resolution (≈ 10^{-5} sec) for the necessary kinetic measurements. Perhaps the most compelling reason for using supersonic jets however is the fact that the nucleation kinetics of the highly supersaturated refractory metal atom concentrations needed to obtain adequate metal atom absorption or fluorescence are expected to be rapid; spatially extending the zone of useful atom concentrations by resorting to a supersonic gas flow appears to be needed to make the homogeneous oxidation reaction dominate with optical resolution adequate to determine the rate coefficient.

The temperature of the supersonic jet, i.e. the reaction temperature, is determined by the temperature upstream of the nozzle and the expansion ratio. Using the Mach 3 nozzle and a vacuum furnace temperature of 1600 K would yield reactor temperatures of 570 and 400 K for N_2 and Ar, respectively.† Lower temperatures can be achieved (i) by mixing room temperature N_2 or Ar quench gas in the plenum chamber (Fig. 3) with the metal vapor laden flow from the vacuum furnace prior to the nozzle expansion, (ii) by using lower vaporizer temperatures and (iii) by a combination of both these methods. Reaction temperatures in the 200-300 K range seem readily obtainable by these means. Using a 1600 K vacuum furnace in combination with a Mach 1 nozzle would yield reaction temperatures of 1330 and 1200 K for N_2 and Ar carrier, respectively. Thus the wall-less reactor could be used over a range of temperatures from those used‡ with the high temperature tubular fast flow reactor of Appendix A, down to about 200 to 300 K.

The vacuum furnace metal vaporizer design derives largely from that developed for the present high-temperature fast-flow reactor facility (Appendix A) and thus entails a maximum transferral of expertise from one apparatus to the other. Points in which the designs differ importantly are:

i) The wall-less reactor unit is to be horizontal, facilitating a smooth unobstructed channel flow and permitting an easy traverse of the apparatus' optical system (i.e., hollow cathode light source, vibrating slit chopper, condensing lens and monochromator-plus-photomultiplier detector) along horizontal guides. To prevent sagging of the alumina vaporizer tube and heat shields, alumina supports will be provided at intervals of 38 cm. With McDanel 998 alumina so supported no problems whatever are anticipated (by the

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† The governing equations are[13]:

$$T_u/T_d = 1 + 0.5(\gamma - 1)M^2$$

and

$$P_u/P_d = \left[1 + 0.5(\gamma - 1)M^2\right]^{\gamma/(\gamma-1)}$$

in which the subscripts u and d indicate upstream and downstream from the nozzle, γ is the ratio of specific heats of the bath gas and M the downstream Mach number.

‡ In principle the tubular reactor can also be used at temperatures down to 200 K. Studies at 300 K have in fact been the main use of this type of reactor. However, in the use of refractory metals such as Fe and Al, 1000 to 1200 K appears to be a lower useful limit. Our high temperature reactor was built expressly to (i) allow making the first tubular flow reactor measurements of any kind in the 1000 - 2000 K range and (ii) facilitate the study of high boiling (low vapor pressure) metals.

manufacturer)[14] up to about 1800 K; it is anticipated that sagging will begin to be a small but manageable problem at about 1900 K, which accordingly will be close to the upper temperature limit of use for the vacuum furnace/vaporizer.

ii) No observation ports need be drilled through the ceramics used in the wall-less facility, greatly strengthening the ceramic tubing employed.

iii) To permit use of gas flows up to about 1000 ml(STP) sec^{-1}, the maximum power consumption for the new apparatus should be increased to 15.6 kVA (from 9.5 kVA on the present reactor), with 50 A and 104 V per zone. Additionally, the Pt-40% Rh elements are to be wound on the (grooved) central core, as in the most recent improvement to the present fast flow reactor facility (cf. Section II. A. 1.).

Other specific points to note about the design are:

1. Interchangeable contoured nozzles can readily be employed, permitting flexibility in area expansion ratios, and hence in reactor temperatures and pressures attained with perfectly expanded jets. Flow visualization can readily be achieved (by subjecting the N_2 quench to a discharge before admitting it to the plenum, thus establishing that the flow is correctly expanded).

2. Oxides and residual metal vapors diffusing out of the reacting gas flow will be swept out of the reactor by means of an N_2 sweeper flow, much as in the present facility.

3. Because the walls of the facility are relatively far-removed from the reacting gas flow, and are cool, the use of conventional observation windows is readily feasible.

4. In addition to the ability to traverse the optical system, the O_3/O_2 inlet as well will be traversable (either by means of a slide plate, or by means of a rod linked to the inlet and traversed from the end of the reactor). Thus the oxidizer inlet may be traversed relative to a fixed observation axis to spatially resolve the kinetics, as in the high temperature reactor, or the optics may be traversed independently, an option not possible in the high-temperature fast-flow reactor facility.

B. Method of Data Interpretation

Interpretation of data obtained from the wall-less reactor facility will be much the same as that of data obtained from the present apparatus with the exception that nucleation will represent an additional process by which metal atoms are depleted from the gas flow; furthermore, diffusion of metal vapor from the supersonic flow will supplant heterogeneous oxidation at the walls of the reactor as a radial loss process. Thus

$$a = \frac{-d \ln [Me]}{dx} = a_{Ox} + a_{Diff} + a_{Nucl} \qquad [A]$$

i.e., the observed metal atom depletion rate is the sum of the rates of homogeneous oxidation (a_{Ox}), a radial diffusion (a_{Diff}) and nucleation (a_{Nucl}).

As previously discussed (Appendix B, p. 7)

$$a_{Ox} = k_{Ox}[Ox]/\eta v \qquad [B]$$

where k_{Ox} is the homogeneous oxidation rate coefficient, $[Ox]$ is the concentration of oxidizing species (O_3 or O_2), η is a term on the order of 1.3 and v is the gas bulk velocity. †

Similarly,

$$a_{Diff} = \frac{k_{Diff}}{v} \approx \frac{23 D}{d^2 v} \qquad [C]$$

where k_{Diff} is the effective pseudo-first order laminar rate coefficient for radial diffusion, D is the metal atom diffusivity in the jet and d is the jet diameter.

The facility will be operated at very low metal atom concentrations, much as is the present flow reactor, to suppress metal nucleation rates. If we make the reasonable postulate that at very low metal atom concentrations the rate-limiting step in initiating metal atom removal by nucleation is the rate of formation of dimers, i.e.,

$$Me + Me \xrightarrow{k_{Nucl}} Me_2 \rightarrow \text{Particles} \qquad (3)$$

where k_{Nucl} may involve a third body, and may correspond either to homogeneous or heterogeneous nucleation, then

$$a_{Nucl} = \frac{k_{Nucl}[Me]}{v} \qquad [D]$$

From Eq. [A] it is evident that the planned facility will be useful in studies of k_{Ox} only if $a_{Ox} > (a_{Diff} + a_{Nucl})$, and useful in studies of nucleation (in which $[Ox]$ will be zero) only if $a_{Nucl} > a_{Diff}$. That these inequalities can

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† In Eq. [B], the correction for axial diffusion has been omitted since this term is negligible in supersonic flows.

readily be satisfied in principle is easily demonstrated:

For illustrative purposes, consider Al/Ox oxidation in a 2 cm diam Mach 3 Ar jet at 400 K and 1 Torr. Assume $k_{Ox} \approx 1 \times 10^{-10}$ ml particle^{-1} sec^{-1}, $[Ox] \approx 2.4 \times 10^{14}$ ml^{-1} (corresponding to 1.0 mole percent) and $[Al] \approx 10^{13}$ ml^{-1} (corresponding to $\approx 90\%$ absorption). Under the assumed representative flow conditions, $v = 1.1 \times 10^5$ cm sec^{-1} and $D_{Al} \approx 500$ cm^2 sec^{-1}. k_{Nucl} is unknown but may be estimated† as on the order of 5×10^{-10} ml particle^{-1} sec^{-1}. Substitution of these values in Eqs. [B], [C] and [D] leads to the following values of a_{Ox}, a_{Diff} and a_{Nucl}:

$$a_{Ox} = \frac{1 \times 10^{-10} \times 2.4 \times 10^{14}}{1.3 \times 1.1 \times 10^5} = 0.17 \text{ cm}^{-1}$$

$$a_{Diff} = \frac{23 \times 500}{4 \times 1.1 \times 10^5} = 0.026 \text{ cm}^{-1}$$

$$a_{Nucl} = \frac{5 \times 10^{-10} \times 10^{13}}{1.1 \times 10^5} = 0.045 \text{ cm}^{-1}$$

As is evident, the necessary dominance of the metal atom depletion rate by the oxidation reaction can readily be achieved with a reasonable choice of reaction parameters. (Alternatively the nucleation rate could also be studied.) Thus use of the proposed facility to study Fe and Al atom/oxidizer reaction appears to be feasible on all counts. Finally, if a proper vaporizer were to be used the apparatus should be equally useful to the study of metals even less volatile than Fe and Al, such as U.

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† Linevsky[15] has found that k_{Nucl} for FeO and FeOH is on the order of the collision frequency (7×10^{-10} and 3×10^{-10} ml particle^{-1} sec^{-1}, respectively) in low pressure $CO/H_2/O_2$/Air flames. A value of k_{Nucl} higher than the collision frequency cannot be ruled out a priori, but would be quite unexpected.

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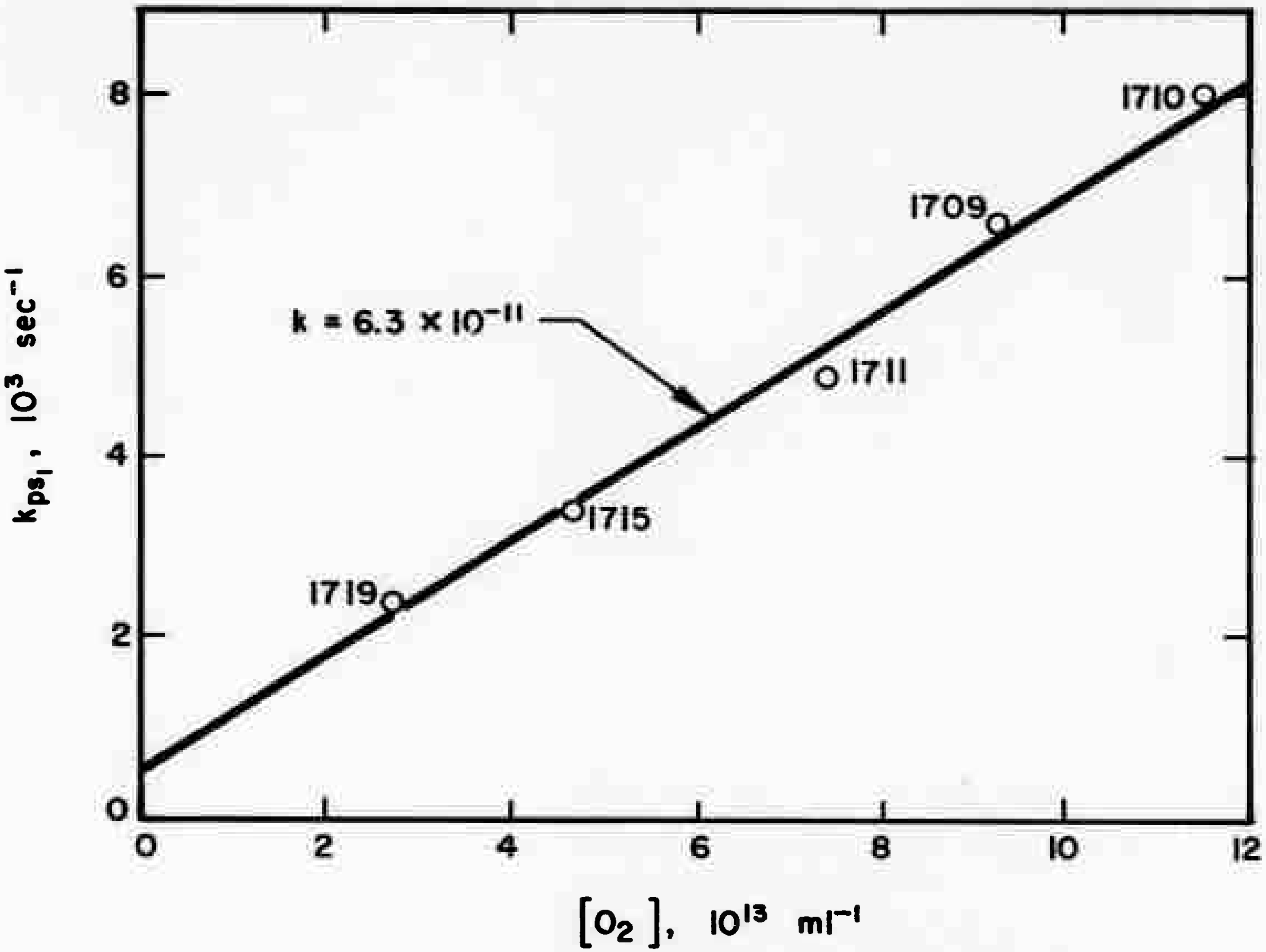

FIG. 1 Al-ATOM CONCENTRATION PROFILE

$\overline{T}$ = 1711 K; $\overline{v}$ = 105 m sec^{-1}; λ = 394.4 nm; P = 10 Torr
The numbers beside the individual data points indicate the measured temperature at that point in the reactor.

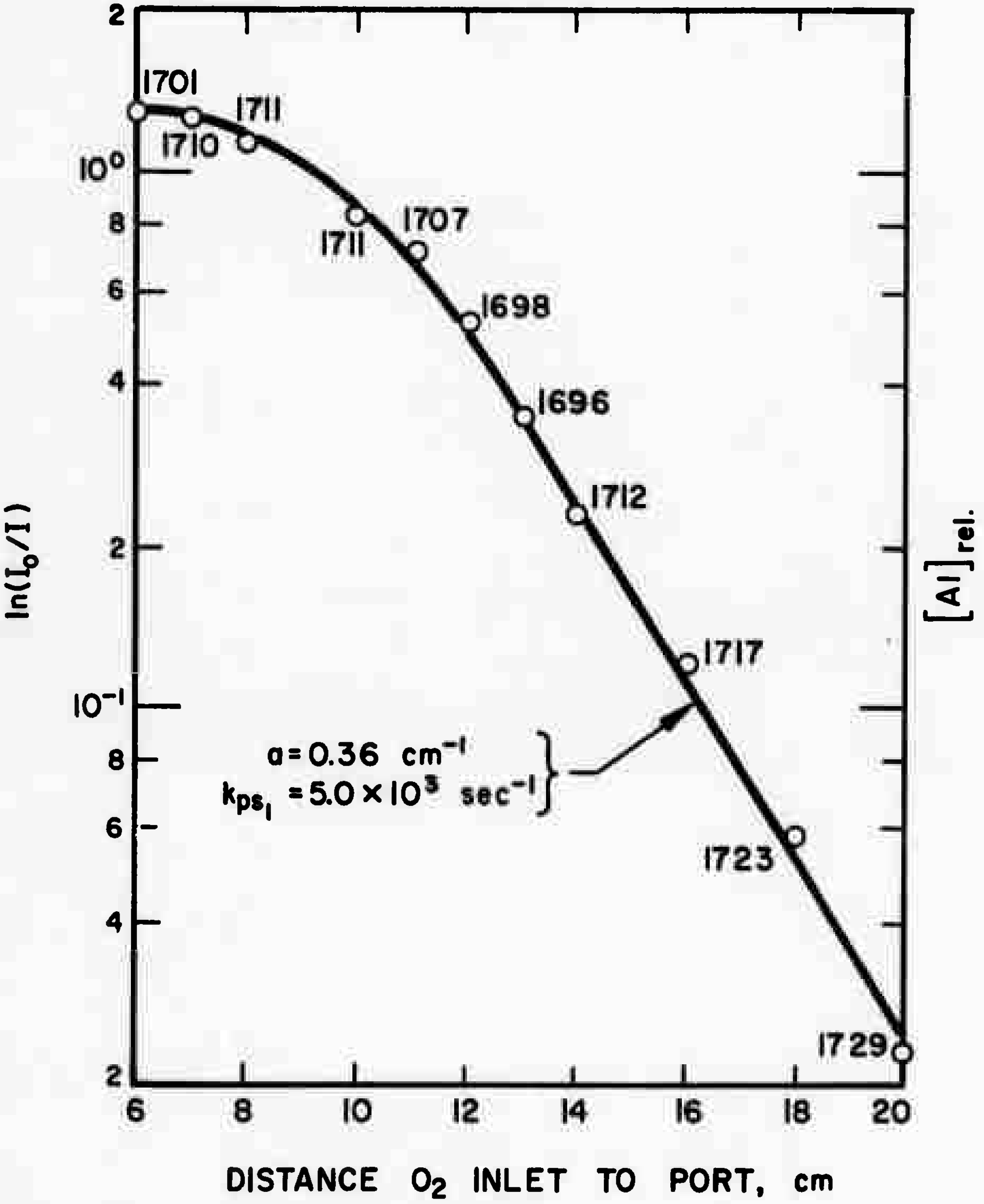

FIG. 2 APPARENT Al/O_2 RATE COEFFICIENT AT 10 TORR

$\overline{T}$ = 1713 K; v = 105 m sec^{-1}; λ = 394.4 nm

The numbers beside each point give the average temperature of the individual runs.

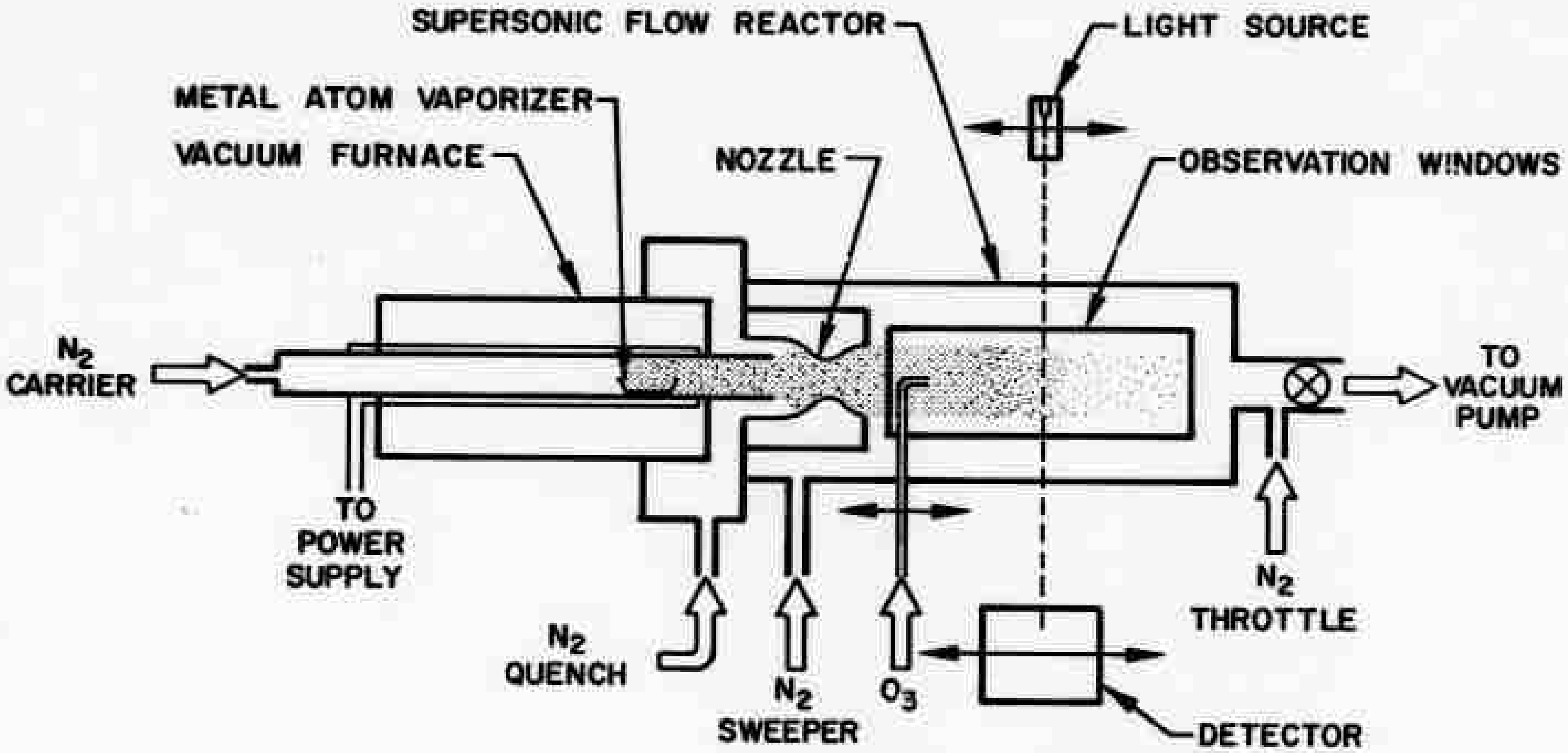

FIG. 3 PLANNED WALL-LESS REACTOR FACILITY

APPENDIX A

TUBULAR FAST FLOW REACTOR FOR HIGH TEMPERATURE GAS KINETIC STUDIES

Arthur Fontijn, Shelby C. Kurzius, James J. Houghton
and John A. Emerson, Review of Scientific Intruments
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Tubular Fast Flow Reactor for High Temperature Gas Kinetic Studies*

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A fast flow reactor suitable for gas kinetic studies at temperatures up to ≈2000 K is described. The reactor has been used in studies of the reactions of atomic Fe and Na with O_2, for which performance data are given.

INTRODUCTION

The conventional tubular flow reactor technique has proved its value for the determination of the mechanism and kinetics of a large number of fast reactions at "low" temperatures (below 1000 K, but mainly at ≈300 K).[1–4] At higher temperatures, kinetic measurements have been obtained only with other techniques, such as those employing flat flames and shock tubes. In this paper we describe a flow tube apparatus suitable for kinetic studies up to ≈2000 K, well above the lower limit of the "high" temperature techniques (≈1000 K). The apparatus was designed to study the kinetics of reactions of refractory atomic species, such as Fe, which could not readily be measured by existing techniques; it also allows for eventual comparisons under like reaction conditions of results obtained by low and high temperature techniques and hence for more reliable measurements of the temperature dependence of rate coefficients. The initial studies made concern the Fe/O_2 reaction at 1600 K and the Na/O_2 reaction at 1200 K.

I. APPARATUS

A. Principle and General Description

The flow reactor is a high purity alumina cylindrical tube situated inside a vacuum furnace. The reactor and vacuum jacket have ports for optical observations. The metal is vaporized and entrained in an inert carrier gas stream. The O_2 is introduced into this gas stream at concentrations several orders of magnitude larger than that of the metal atoms. The basic measurement is that of relative metal atom concentration, which is obtained via optical absorption of the requisite metal atom line emitted by a hollow cathode lamp. Rate coefficients are obtained from the observed variations of this concentration as a function of reaction time, O_2 concentration, and total pressure.

A simplified drawing of the apparatus is shown in Fig. 1. The 2.5 cm i.d. reaction tube is contained inside a 25 cm i.d., 95 cm long vacuum chamber. An inert bath gas (N_2 or Ar) flows through the reaction tube and entrains metal vapor either from a resistively heated basket containing the metal (as in the Na study) or from an internally resistively heated sleeve of the metal to be vaporized (as in the Fe study). O_2 is introduced from the downstream end of the apparatus through a nozzle located at the end of a movable tube. The reaction time is proportional to the distance from this nozzle to the observation port and is varied at a prescribed average gas velocity by changing the nozzle position. The vacuum furnace is continuously purged with the aid of a sweeper gas flow.

B. Vacuum Furnace and Flow Reactor

1. Structure

The essential features are shown in Fig. 2. The vacuum chamber A is a 25.0 cm i.d. brass cylinder, 95.0 cm long, closed at both ends by demountable flanges B_1 and B_2. The 3.2 cm o.d., 2.5 cm i.d. flow reactor C is made of McDanel 998 alumina tubing (99.8% Al_2O_3). At the downstream end the reactor extends into a 3.8 cm i.d. brass tube, which is part of the vacuum jacket. To allow for thermal expansion and induce the sweeper gas to flow through the observation ports, an asbestos fiber collar W provides a flexible—but pervious—seal between the reactor and the brass tube. The muffle (with three contiguous heating zones) D is composed of a grooved (with 0.8 cm pitch) 5.1 cm o.d., 4.5 cm i.d., 82 cm long McDanel 998 alumina core, wound with 0.127 cm diam Pt-40% Rh resistance wire. The end zones and the central zone are each wired separately to maintain a nearly uniform temperature over the 30 cm portion of reaction tube in which measurements are made. The windings are protected with three thin coats of alumina base cement (Aremco Ceramabond 503) and are each shielded by a 25 cm long, 6.0 cm o.d., 5.4 cm i.d. McDanel 998 alumina tube. The core is held in place by two stainless steel disks E_1 and E_2 (20 cm diam), which are fastened together by the rods Q_2. These disks have grooves which seat the core and three cylindrical radiation shields F. The innermost—and hottest—shield is a 75 cm long, 11.4 cm o.d., 10.5 cm i.d. length of McDanel AV 30 alumina tubing (96% alumina). Molybdenum sheet (0.05 cm thick) is used for the two outer shields. The entire muffle assembly is supported by rods Q_1 connecting the top disk E_1 to the end plate B_1 of the vacuum housing A. By means of a hoist on the ceiling the whole furnace can be removed for inspection or repair. The entire vacuum chamber is surrounded by coiled copper tubing G through which cooling water flows.

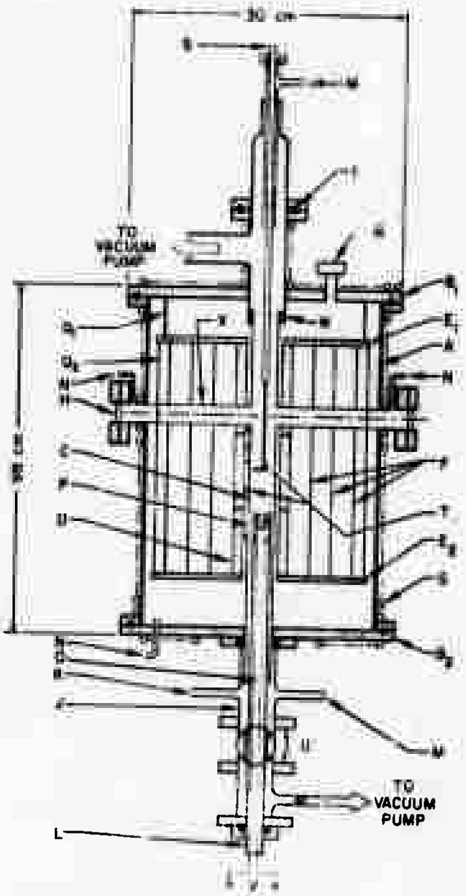

Fig. 2. Vacuum furnace and flow reactor. A—Vacuum jacket, B—flange, C—reaction tube, D—heating element (resistance wire and its connections not shown), E—supporting disk, F—radiation shield, G—cooling coil, H—window, I—O-ring seal, J—connecting cross, K—N_2 or Ar inlet, L—support tube for heated crucible assembly, M—manometer outlet, N—sweeper gas inlet, O—crucible power leads and thermocouple assembly, P—heated crucible, Q—support rod, R—vacuum feedthrough for the thermocouples situated on the outside of the reactor, S—O_2 introduction system, T—thermocouple, U—ball valve, V—vaporizer power supply, W—asbestos fiber collar, X—sight tube.

The optical path for the measurement of the relative metal atom concentration by light absorption is provided by two 2.5 cm diam quartz windows in the vacuum jacket, which are aligned with 2.5 cm diam holes in the radiation shields and the muffle and the 1.2 cm diam open ports of the reaction tube. A bottom flange seals the reaction tube to the vacuum jacket base flange B_2. (All conjoining flanges are sealed via O-rings.) Silver-brazed to the bottom flange is a stainless steel cross tube J, which provides the inlet K for the bath gas and connections to the 3.2 cm i.d. ball valve U and manometers M. The 1.9 cm o.d. alumina support tube L for the resistively heated vaporizer P can readily be withdrawn through the ball valve, thus permitting closure of the valve and complete isolation of the vaporizer from the reactor. This valve greatly facilitates making repairs to and replenishing the vaporizer without otherwise altering furnace conditions.

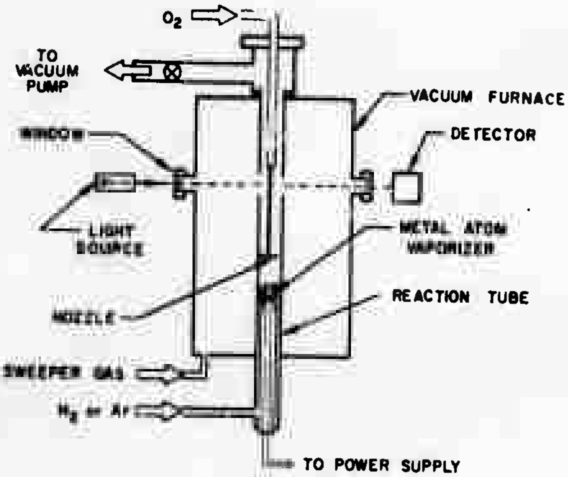

Fig. 1. Schematic of apparatus.

To eliminate irreversible signal degradation otherwise encountered due to fogging, the reactor observation ports are operated without windows. The optical path external to the reactor is continuously swept free of metal vapors with a flow of inert gas admitted directly over the inside of the jacket windows. Sweeper gas also enters the vacuum jacket at its base. The inlets N and alumina sight tubes X are used for these purposes.

The upper useful temperature limit of the apparatus as presently constructed is fixed by the 2040 K and 2220 K maximum operating temperatures[5,6] of the Pt-40% Rh resistance wire and of the high purity alumina tubing, respectively.

2. Temperature Control and Measurement

The power supplies for each of the three heating zones are independently controlled. Each supply consists of a step-down transformer, a solid state rectifier, a rheostat, and a current meter. A 0.05 cm diam Pt/Pt–10% Rh thermocouple is situated on the outside wall of the reactor opposite the center of each of the three heating zones. To permit taking a rapid approximate scan of the reactor temperature profile two additional thermocouples are utilized, with the result that external reactor temperature measurements can be made 2, 7, 12, 24, and 42 cm upstream of the observation port. The leads for these fixed thermocouples are fed through the top of the vacuum jacket via the vacuum feedthrough R. The maximum power consumption is approximately 9.5 kVA, with 45 A and 70 V per zone. The temperature of the reactor gas stream is measured by a 0.025 cm diam Pt/Pt–10% Rh thermocouple adjacent to the movable O_2 nozzle with leads fed through the stainless steel tube S (Fig. 2 and Sec. I.C. 3).

3. Pressure Control and Measurement

The pressure is continuously indicated by an Alphatron pressure gauge and is measured absolutely by one of three manometers; all pressure indicators are connected in parallel to the manometer outlets M. These outlets are situated upstream and downstream of the reactor to check that the pressure drop across the reactor is not significant. The manometers are (i) for the 0.05–4 Torr range, a precision U-tube dibutylphthalate oil manometer[7]; (ii) for the 4–50 Torr range, a precision U-tube mercury manometer[7]; and (iii) for higher pressures, a conventional mercury manometer. Pressure at a given flow rate is controlled by a throttling valve in the line to the 3.68 $m^3 min^{-1}$ vacuum pump.

4. Precautions

The system has been used continuously for several weeks-long periods. With our earlier designs frequent failures were encountered. This problem has been surmounted by the present construction and the following precautionary measures which are observed in addition to those normally employed in working with ceramics at high temperatures.[5]

Sensing devices are interlocked with the furnace power supply in such a way that, in the event of a major pressure leak, a power failure, or a cooling water supply interruption, the heating elements are automatically turned off. The interlock system is reset automatically for short power interruptions (<30 min). Otherwise, the temperature must be raised gradually by the operator. These features are highly desirable for the periods of unattended operation of the furnace, which is kept continuously at high temperatures.

Heating element burn-outs caused by Pt/Rh vaporization losses and chemical attack by metal vapors are minimized by (i) the protection provided by the alumina base cement coating the heating elements, (ii) addition of $\approx 1\%$ O_2 to the sweeper gas to provide a slightly oxidizing environment in the furnace,[6] and (iii) maintaining the apparatus at ≈ 40 Torr and ≈ 1100 to 1300 K when not in operation. The latter precaution also minimizes thermal stress-related problems of the windings and the alumina structural elements.

C. Metal Atom and O_2 Introduction Systems

1. Fe Introduction

The Fe study has been performed at a reaction temperature of 1600 ± 30 K. At this temperature the equilibrium saturation vapor pressure of Fe is $\approx 10^{-3}$ Torr,[8,9] corresponding to $[Fe] \approx 6 \times 10^{12}$ ml^{-1}, which is sufficient to give greater than 90% absorption of the Fe I 248.3 and 372.0 nm lines. Since 1600 K is considerably below the melting point of Fe (1809 K),[8,9] it is not necessary to heat the Fe to its melting point to obtain an adequate gas phase Fe–atom concentration. The Fe is therefore evaporated simply by using an inverted pure Fe beaker, 4.1 cm long, 1.2 cm o.d., 1.0 cm i.d. This beaker is resistively heated from within, using 0.08 cm diam W wire wound over a 0.5 cm o.d., 0.2 cm i.d. alumina tube. The W-wound ceramic fits snugly into an alumina liner (0.95 cm o.d., 0.7 cm i.d.) placed into the Fe beaker. This assembly is placed directly inside the reaction tube on top of the open-ended 1.9 cm o.d., 1.6 cm i.d. alumina support tube L, Fig. 2, movable in the axial direction.

Power for the beaker assembly is provided through 0.25 cm diam Mo rods containing 1.0 cm long, 0.09 cm diam holes into which the W heating wire ends are fitted. A Pt/Pt–10% Rh thermocouple is embedded in alumina cement in a notch cut in the center of the Fe beaker. This thermocouple is used for manual control of the Fe beaker temperature.

With a new beaker, a stable Fe–atom flow is obtained with a heating current of ≈ 10 A, corresponding to a temperature approaching 1800 K at the center of the beaker. In operation the beakers slowly begin to sag; iron is denuded from the middle and deposits on the relatively cool downstream end. As a result the heating current gradually has to be increased to ≈ 20 A and the beakers have to be replaced after about 20–25 h of use.

2. Na Introduction

Sodium, like many other metals of interest, is a liquid at temperatures high enough to provide atomic vapor concentrations yielding ≈90% absorption of the 589 nm line in the present apparatus. An Na introduction procedure somewhat different from the method used for Fe therefore is required: Na is contained in a 1.2 cm long, 1.0 cm i.d. alumina crucible (with attached Pt/Pt–10% Rh thermocouple) placed on top of tube L. To obtain a readily adjustable constant Na concentration we have found it necessary to control the crucible temperature independently, rather than use the reactor heat alone. This control is achieved by positioning the crucible at a point in the reactor where the temperature is ≈400 K, i.e., above the melting point of Na but somewhat below the required ≈500 K. This temperature (i.e., ≈500 K) is then obtained by resistively heating the crucible with 0.05 cm diam W wire which surrounds and supports it.

3. O_2 *Introduction*

The O_2 flows through a 0.16 cm i.d. alumina tube extended from a mating stainless steel tube S (Fig. 2). This tube is offset 0.6 cm laterally from the center axis of the reaction tube, so that it does not block the radiation used in measuring the relative metal atom concentration, and can be moved axially through sliding O-ring seals to vary the reaction time. To uniformly distribute the O_2 over the reactor cross sectional area a multihole ring distributor is attached to the tip of the tube. The ring is formed of 0.13 cm i.d. Pt–10% Rh tubing, with a 0.013 cm wall thickness, bent to a 1.2 cm i.d. circle. The twelve ≈0.08 cm diam inlet holes are situated in a plane perpendicular to the reactor axis on a hexagonal pattern along the inner and outer circumference of the ring.

The O_2 nozzle can be moved over the entire 30 cm portion of the reactor upstream from the observation port in which measurements are made.

D. Optical System

Westinghouse high spectral output Ne-filled hollow cathode Fe or Na lamps, powered by a stabilized (±0.1%) current-regulated dc supply, are used as light sources. The light from the lamp is sent through a vibrating (140 Hz) slit chopper and then passes through the reactor. A condensing lens focuses the radiation on the entrance slit of a monochromator equipped with standard side-on photomultiplier tubes, the output of which is measured with a phase-sensitive amplifier.

II. OPERATION

A. Procedure

Gas handling procedures similar to those used in our room temperature conventional fast flow reactor studies (see, e.g., Ref. 7) have been employed. Reaction tube gas volume flow rates used are on the order of 100 to 400 ml (STP) sec^{-1}. A sweeper gas volume flow rate of about one-tenth that of the reaction tube flow rate is passed through the furnace and sight tubes. The flow of sweeper gas into the reactor at the observation ports does not interfere with our ability to make metal atom oxidation rate measurements, since these measurements are based on the observed change in reactant concentration as a function of reaction time when the O_2 nozzle is moved between points well upstream from the ports. The validity of operating in this manner has been demonstrated previously by other workers[4,10] concerned about having the measurement station at a point downstream from the useful observation zone at different reaction conditions. We have, further, found it useful to add ≈1% O_2 to the sweeper gas (i.e., ≈0.1% of the reactor gas flow) to chemically scavenge residual vapors in the furnace; as already noted above, this slightly oxidizing atmosphere is also beneficial for the Pt–40% Rh resistance wire.

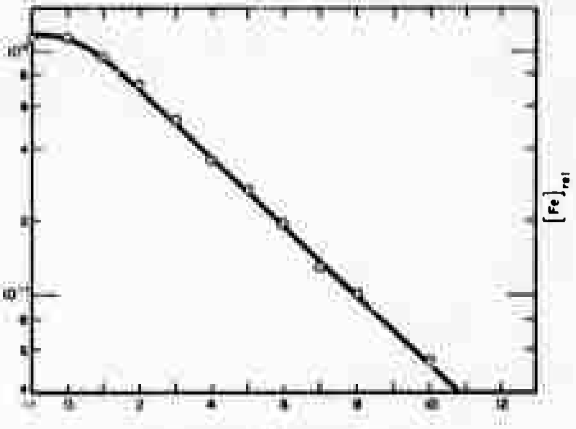

FIG. 3. Metal atom concentration profile: Fe/O_2 reaction. $\bar{T}=1589$ K, $\bar{v}=48.6$ m·sec^{-1}, $[O_2]=0.89\times10^{15}$ ml^{-1}, $\lambda=372.0$ nm, $P=15$ Torr.

The 248.3 and 372.0 nm Fe I lines and the 589 nm Na I D line have been used in the optical absorption measurements. The relative metal atom concentration [Me] is obtained using the Lambert–Beer absorption law in the form $[Me]\propto \ln I_0/I$, where I_0 and I are the respective light intensities in the absence and presence of metal atoms in the light path. To ascertain that these absorption measurements are not influenced by other factors (e.g., the presence of nucleated products) the intensity of the 585.2 nm Ne I line, emitted by the hollow cathode lamp, is routinely monitored. No attenuation of this line has been observed.

Temperature at each fixed station on the outside of the reaction tube remains constant to within ±5 K during experiments; temperature differences measured along the reaction tube axis were ≈±25 K. A stronger temperature drop occurs close to the observation port, which acts

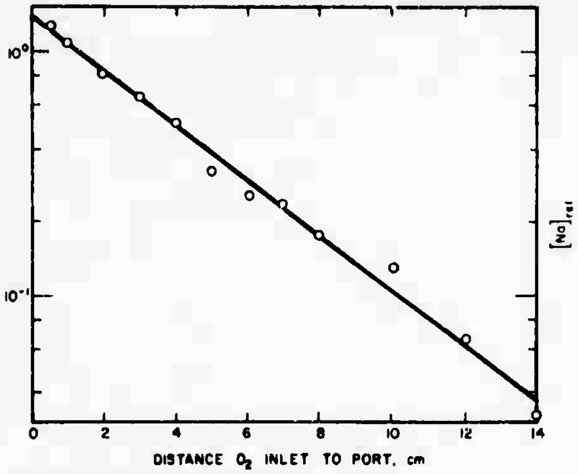

FIG. 4. Metal atom concentration profile: Na/O_2 reaction. $\bar{T}$ = 1176 K, $\bar{v}$ = 9.34 m·sec^{-1}, [O_2] = 65.1×10^{16} ml^{-1}, λ = 589.0 nm, P = 200 Torr.

effectively as a heat sink in a radiant enclosure. In addition to flow disturbances near the ports (see above), this was a reason to give little weight to the data obtained close (i.e., 1 to 2 cm) to the ports. $\bar{T}$ is taken as the integrated mean of the centerline thermocouple readings over the linear region of the reaction zone in plots such as in Figs. 3 and 4 and is reproducible within ±10 K from run to run.

B. Measurements

The most extensive measurements so far have been made on the homogeneous gas phase Fe/O_2 reaction at 1600 ±30 K. The range of experimental parameters explored for this system is λ—248.3 and 372.0 nm, P—15-60 Torr, bath gas—N_2, [O_2]—0.1-10.3×10^{15} ml^{-1}, mean gas velocity $\bar{v}$—21-110 m·sec^{-1}. All experiments were run under conditions such that [O_2]≫[Fe], i.e., pseudo-first-order reaction conditions prevailed. Initial experiments were made at 3 Torr. At this pressure wall oxidation was found to be dominant, i.e., the observed reaction was of first order in [Fe] and of zeroth order in [O_2].

Figures 3 and 4 show typical pseudo-first-order plots of the measured relative metal atom concentrations as a function of distance. Interpretation of the slope of these plots to yield reaction rate coefficients is a standard procedure entirely the same as is used for flow tube data collected at lower temperatures (see, e.g., Refs. 1 and 11). For the gas phase $Fe+O_2 \rightarrow FeO+O$ reaction at 1600 K a rate coefficient of (3.6±1.4)×10^{-13} ml molecule^{-1} sec^{-1} was obtained; detailed results are presented elsewhere.[12] The experiments made at 3 Torr allowed us to obtain a lower limit estimate of the oxidation probability per Fe collision with the wall in the presence of O_2, $\gamma_{Fe,1600\,K} \geq 10^{-1}$. Although more extensive Na experiments are yet to be made, the data obtained so far yield a rate coefficient for the reaction $Na+O_2+M \rightarrow NaO_2+M$ on the order of 10^{-32} ml^2 molecule^{-2} sec^{-1} at 1200 K. Experiments at 1 Torr indicate for the Na/O_2 system a fast wall oxidation reaction, $\gamma_{Na,1200\,K} \approx 10^{-2}$, significantly slower than that of Fe.

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APPENDIX B

HIGH-TEMPERATURE FAST-FLOW REACTOR STUDIES OF METAL ATOM OXIDATION KINETICS

Arthur Fontijn, Shelby C. Kurzius and James J. Houghton, Fourteenth Symposium (International) on Combustion (to be published), AeroChem TP-277, March 1972

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HIGH-TEMPERATURE FAST-FLOW REACTOR STUDIES OF METAL ATOM OXIDATION KINETICS

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Summary

The tubular fast-flow reactor, previously used for reaction kinetic measurements at temperatures up to only 1000 K, has been adapted to reach temperatures up to 2000 K and has been applied to studies of gas phase reactions of metal atoms with O_2. The most extensive set of results obtained so far is for the Fe/O_2 reaction in an N_2 bath at 1600 K. This reaction proceeds via $Fe + O_2 \rightarrow FeO + O$ with a rate coefficient of $(3.6 \pm 1.4) \times 10^{-13}$ ml molecule^{-1} sec^{-1}. Evidence has also been obtained for a wall oxidation reaction for which $\gamma_{Fe, 1600 K} \geq 10^{-1}$. Preliminary results for the Na and Al reactions with O_2 at 1200 and 1700 K, respectively, are discussed. The experimental technique described here allows measurements to be made under reaction conditions overlapping those used in flame and shock-tube studies.

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[†] Prepared for the Fourteenth Symposium (International) on Combustion.

Introduction

Studies of metal combustion rates have been largely confined to environments where either heterogeneous oxidation predominates or where an unknown combination of homogeneous and heterogeneous processes occurs. Such studies have been performed mainly on bulk metal surfaces (e.g. Ref. 1), on burning droplets (e.g. Ref. 2), and with metallized propellants (for general references see Refs. 3-6). Work has been performed also with shock-heated suspensions of droplets (e.g., Ref. 7) and metal vapor diffusion flames (e.g. Refs. 8, 9). Even in the latter systems, reaction rates may strongly depend on the presence of a fog, or smoke, of oxide particles.[10] As a consequence homogeneous rate coefficients of metal vapor oxidation are mostly unknown, in spite of the important role such processes are thought to play in the combustion of several metals,[11] in the upper atmosphere (e.g. Refs. 12 and 13), in refractory vapor deposition,[14] and in the emission of metallic air pollutants from mobile combustion sources and such stationary sources as smelters and electric utility fossil fuel burners (see, e.g., Ref. 15).

A number of previous studies have been aimed specifically at obtaining homogeneous metal atom oxidation kinetics free from the complexities of a condensed phase. Carabetta and Kaskan[16] and McEwan and Phillips[17] have measured alkali atom/O_2 kinetics in premixed $H_2/O_2/N_2$ flames. Linevsky,[18] also employing premixed flames, found that the kinetics of the Fe/O_2 reaction could not be measured in such a medium because of the rapidity of back reactions. Evidence for such fast back reactions has also been obtained[19] in an upper atmospheric release where oxidation of $Fe(CO)_5$ led initially to FeO which was rapidly converted by reaction with ambient O atoms to Fe. Attempts at measuring homogeneous kinetics in shock tube studies, where the metal atoms were to be provided from finely dispersed Mg and Al metal droplets, have not succeeded thus far.[7,20] In another shock tube study,[21] free Fe atoms were successfully obtained by decomposition of $Fe(CO)_5$ at temperatures of 2400 K and greater; however, the Fe/O_2 reaction rate was found to be too fast to measure under these conditions, though an approximate lower limit to the rate coefficient was measured.

The need for an alternate technique for studying refractory vapor oxidation kinetics is apparent both for systems where no present technique suffices and for systems where existing techniques appear adequate but where a check by an independent technique is particularly desirable. An a priori good candidate is the conventional cylindrical fast-flow reactor technique. This technique has made possible the measurement, in well-identified reaction environments, of the kinetics of a large number of reactions--primarily of O, N, H and halogen atoms and free radicals such as OH--in the 200 to 1000 K range. Ryason and Smith[22] have recently used the technique for measuring the oxidation rate of a relatively volatile metal (Pb), at temperatures up to 990 K in a quartz fast-flow reactor. We have now constructed a tubular alumina fast-flow reactor housed in a vacuum furnace, suitable for studies up to ≈ 2000 K, and thus useful for kinetic measurements involving vapors of refractory species. The first detailed study with the reactor is reported here and concerns the reaction

$$Fe + O_2 \rightarrow FeO + O \tag{1}$$

for which a rate coefficient of $(3.6 \pm 1.4) \times 10^{-13}$ ml molecule^{-1} sec^{-1} at 1600 K has been measured. Data are also reported on the reactions of Na and Al with O_2.

Experimental

A detailed description of the apparatus and its operation is given elsewhere;[23] a simplified drawing is shown in Fig. 1. The 2.5 cm i.d. alumina reactor is contained inside a 25 cm i.d., 95 cm long, vacuum chamber. A 5.1 cm o.d. alumina muffle tube and a number of alumina and molybdenum heat shields (not shown) surround the reactor. The muffle is wound with Pt-40% Rh resistance wire. The upper temperature limit, nearly 2000 K, is determined by the construction materials of the reactor. Bath gas (N_2) passes through the reactor and entrains atomic metal vapor. In the case of Fe the vapor has been supplied from an Fe sleeve which surrounds a resistance heater; this configuration is possible since sufficient Fe vapor sublimes from Fe below its melting point. Atomic Na and Al have been supplied from crucibles containing the molten metals. O_2 is introduced from the downstream end of the apparatus through a multi-hole ring-shaped Pt-10% Rh nozzle located at the end of a movable alumina tube. The reaction time is proportional to the distance from this nozzle to the observation port and is varied by changing the nozzle position. Relative metal atom concentrations, $[Me]_{rel}$, in the gas passing the observation port are measured by absorption of chopped metal atom radiation from Ne-filled Westinghouse hollow-cathode lamps. To allow these optical measurements, the O_2 inlet tube is offset 0.6 cm laterally from the reactor axis. The intensity of the Ne I 585.2 nm line from the lamps is routinely monitored to ascertain that optical absorption measurements of $[Me]_{rel}$ are not influenced by extraneous factors.

(continued on following page)

To quickly obtain an indication of the temperature profile along the reactor, five thermocouples are situated at fixed stations on the outside wall of the reactor. The temperature of the gas stream within the reactor is measured by a 0.025 cm diam Pt/Pt-10% Rh thermocouple adjacent to the movable O_2 inlet. The following temperature observations pertain to the Fe/O_2 system at about 1600 K: The gas stream temperature is about 20 K lower than at the corresponding fixed stations on the outer reactor walls. Temperature at each fixed station remains constant to within ± 5 K during experiments; temperature differences along the useful length (about 30 cm) of the reaction tube are ± ≈ 25 K. A larger temperature drop occurs close to the observation port, which acts as a heat sink in a radiant enclosure. For this reason and because of flow disturbances near the ports (see below) data obtained close to the ports are rejected. $\overline{T}$ is taken as the integrated mean of the gas stream temperatures over the linear region of the data plots, (e.g. 1 - 10 cm in Fig. 2). $\overline{T}$ is reproducible within ± 10 K from run to run (cf. Fig. 3).

Pressure measurement stations are located upstream and downstream of the reactor. Over the range of conditions covered, i.e. from 1 to 300 Torr, no pressure drop (i.e. $\Delta p \leq 0.2$ Torr) along the length of the reactor is observed. Routine[24] gas handling procedures are used. Nitrogen is obtained directly from a liquid N_2 container. Linde U.S.P. O_2 is dried by passage over activated alumina. Ar was used as the bath gas in a few experiments in which it was established that N_2 does not react with Fe, Al or Na at a measurable rate under the conditions of our experiments.

To prevent the reaction gases from entering the vacuum jacket through the reaction tube ports, N_2 sweeper gas, at a volume flow rate of about one tenth that of the reaction tube flow rate, is passed through the furnace. The flow of sweeper gas into the reactor at the observation ports does not interfere with our ability to make metal atom oxidation rate measurements, since these measurements are based on the change in reactant concentration as a function of reaction time when the O_2 nozzle is moved between points well upstream from the observation point. The validity of operating in this manner has been demonstrated by other workers[25,26] using fast-flow reactors with the measurement station at a point downstream from the useful observation zone, at different reaction conditions.

Method and Data Interpretation

The methods for determining rate coefficients from cylindrical fast-flow reactor experiments are well established from lower temperature work (see, e.g., Refs. 27 and 28). In the present work the rate coefficients for $Me/O_2/(M)$ reactions have been determined from the variation in $[Me]_{rel}$ as a function of reaction time, O_2 concentration, and total pressure, for conditions such that $[O_2] \gg [Me]$ to allow a pseudo-first order interpretation of the data. Results of a representative experiment are shown in Fig. 2. In this figure, the measured quantity $\ln(I_0/I)$ has been plotted on semi-logarithmic co-ordinates versus the distance of the O_2 inlet upstream of the observation port centerline. Since $[\mathrm{Me}]_{\mathrm{rel}}$ is proportional to $\ln(I_0/I)$ via the Lambert-Beer law, plots such as Fig. 2 are semi-logarithmic plots of $[\mathrm{Me}]_{\mathrm{rel}}$ at constant values of [M] and $[O_2]$. Kinetic analysis of such data is relatively straightforward for simple plug flow (i.e., for flow with a flat velocity profile) with non-catalytic walls,[27,28] or for simple laminar flow (i.e., for flow with a parabolic velocity profile) with active catalytic walls.[27] As shown by Ferguson et al,[27] sophisticated numerical calculational models which incorporate such departures from ideal behavior as the effects of reactant inlets on the reacting species distribution within the reactor, pressure gradients, axial and radial diffusion, and slip velocity, yield results which are intermediate between the extremes derived from the simple plug and parabolic flow models, which in themselves yield not greatly divergent results. We have evaluated the experimental data in terms yielding the mean result of these models, though a parabolic profile probably is approached in the experiments.

For pseudo-first order disappearance of Me, $-d[\mathrm{Me}]_{\mathrm{rel}}/dt = k_{ps_1}[\mathrm{Me}]_{\mathrm{rel}}$ i.e., $k_{ps_1} = -d\ln[\mathrm{Me}]_{\mathrm{rel}}/dt$. From the local slope, $a = -d\ln[\mathrm{Me}]_{\mathrm{rel}}/dx$, of the data plots (see Fig. 2), the pseudo-first order rate coefficient k_{ps_1} is obtained via the equation

$$k_{ps_1} = \eta a \bar{v}(1 + a D_{\mathrm{Me}}/\bar{v}) \qquad \text{(A)}$$

In Eq. (A) η is a factor equal to 1 for plug flow and approximately equal to 1.6 (Ref. 27) for parabolic flow, $\bar{v}$ is the mean bulk linear gas velocity, D_{Me} is the diffusivity of Me atoms, and $(1 + a D_{\mathrm{Me}}/\bar{v})$ is the correction factor for the effect of axial diffusion,[28] which is small ($\leq 10\%$) for the conditions of our experiments. For our calculations we have taken η to be 1.3 (± 0.3).

The rate coefficient k_{ps_1} incorporates the summation of heterogeneous and homogeneous contributions to the rate, i.e.,

$$k_{ps_1} = k_W + k_I[O_2] + k_{II}[O_2][M] \tag{B}$$

where k_W is the wall contribution and k_I and k_{II} correspond to the binary and ternary mechanisms of Me reaction with O_2, i.e., to the reaction types

$$Me + O_2 \xrightarrow{k_I} MeO + O \tag{I}$$

and

$$Me + O_2 + M \xrightarrow{k_{II}} MeO_2 + M \tag{II}$$

A series of measurements of k_{ps_1} at constant temperature as a function of $[O_2]$ at various constant values of $[M]$ identifies the dominant homogeneous reaction and its rate coefficient.

The Fe/O_2 Reaction

Initial experiments at a pressure of 3 Torr showed that Fe is rapidly consumed upon O_2 addition with a rate which is first order in $[Fe]_{rel}$ and zeroth order in $[O_2]$ over the range $1 \times 10^{12} < [O_2] < 2 \times 10^{13}$ ml^{-1}. These results indicate that a heterogeneous oxidation process takes place. A lower limit for the oxidation probability per Fe-atom collision with the wall,

$\gamma_{Fe, 1600\,K}$, is found to be about 10^{-1} (see Appendix). A definitive determination of this number would require work at appreciably lower pressures to remove diffusional transport limitations which complicate the measurement of γ at 3 Torr. At higher pressures, where the homogeneous oxidation reaction is dominant, the contribution of the wall reaction is evident in the positive intercept of the k_{ps_1} vs. $[O_2]$ plots, cf. Fig. 3.

The 15 - 60 Torr pressure range was found to be convenient for the measurement of the homogeneous reaction. Figure 2 shows a typical first order data plot. The k_{ps_1} values calculated from the data have been plotted against $[O_2]$, cf. Fig. 3, to yield k_1, the second-order rate coefficient. The k_1-data, assembled in Table I, are independent of [M], demonstrating that the predominant Fe-oxidation path is via mechanism (I), i.e.

$$Fe + O_2 \rightarrow FeO + O \qquad (1)$$

The absence of systematic error in the data is evidenced by the independence of the second order rate data from variation in [M], in $\bar{v}$, the average gas velocity, and in the absorption lines used. The linearity of the observed plots and the relative constancy of the results rules out major influences of any other competing processes.

In the experiments, $[Fe] \ll [O_2]$, as required by the pseudo-first order data analysis: The fractional emission line absorption varied from as high as $\approx 90\%$ at the upstream end of the reaction zone to $\approx 1\%$ at the detection threshold. Using recent estimates by Linevsky[18] these figures, for the

372.0 nm line, correspond to $\approx 6 \times 10^{12}$ $ml^{-1} > [Fe] > \approx 3 \times 10^{10}$ ml^{-1}, well below the O_2 concentrations used (Table I). From atomic absorption sensitivity data[29] for the 248.3 and 372.0 nm Fe I lines we estimate the corresponding limits for the 248.3 nm line observations to be 1×10^{12} $ml^{-1} > [Fe] > \approx 5 \times 10^9$ ml^{-1}. Thus the results are also independent of the absolute Fe-concentrations used.

The normalized standard deviation of the determination of k_1 is 22%. Allowing for a possible 20% systematic error and the 23% uncertainty in η, the total uncertainty in k_1 is about 40%. Hence the measured rate coefficient for Reaction (1) is $(3.6 \pm 1.4) \times 10^{-13}$ ml $molecule^{-1}$ sec^{-1}.

While the present technique appears highly suited to the measurement of the temperature dependence of the rate coefficient, such measurements are yet to be made. For the purpose of comparing our results with those obtained by others, an estimate of the activation energy may be made by assuming it to be approximately equal to the estimated[30,31] endothermicity of Reaction (1), 20 kcal $mole^{-1}$. The above results then correspond to $k(T) = 2.0 \times 10^{-10} \exp(-20,000/RT)$. This pre-exponential factor is within a factor of 2 to 3 of the collision frequency rate factor, which makes it unlikely that the activation energy can be appreciably greater than 20 kcal $mole^{-1}$.

The two other attempts at measuring k_1 are those by von Rosenberg and Wray[21] and by Linevsky.[18] von Rosenberg and Wray found in their shock tube work at temperatures of 2400 K and greater that the reaction was too fast to measure, and set an approximate limit $k(2400\ K) \geq$

5×10^{-12} ml molecule^{-1} sec^{-1}, in good agreement with the above k(T) value which yields 3×10^{-12} ml molecule^{-1} sec^{-1} at 2400 K. Linevsky working in lean CO/H_2/air flames at 1500 K, found that due to the rapidity of the exothermic back reaction (-1), an Fe concentration near equilibrium is established, and concluded that $k(1500\,K) \geq 10^{-14}$ ml molecule^{-1} sec^{-1}, also consistent with the present result.

Al and Na Reactions with O_2

Preliminary results for the Al/O_2 reaction at 1700 K indicate a rapid reaction, probably

$$Al + O_2 \rightarrow AlO + O. \qquad (2)$$

The rate constant k_2 is on the order of 10^{-10} ml molecule^{-1} sec^{-1}, consistent with that expected for an approximately thermoneutral[30,32] simple abstraction reaction. There are no other known measurements of k_2.

The data obtained thus far for Na/O_2 yield a rate coefficient for the reaction

$$Na + O_2 + M \rightarrow NaO_2 + M \qquad (3)$$

on the order of 10^{-32} ml^2 molecule^{-2} sec^{-1} at 1200 K. Additionally, a fast wall-oxidation is observed in the Na/O_2 system: $\gamma_{Na,\,1200\,K} \approx 10^{-2}$, significantly slower than that of Fe. The present value for k_3 is comparable to but somewhat higher than the lean $H_2/O_2/N_2$ flame measurements of McEwan and Phillips[17] (2.0×10^{-33} ml^2 molecule^{-2} sec^{-1}; T = 1380 to 2030 K) and about an order of magnitude higher than that of Carabetta and Kaskan[16] (0.8×10^{-33} ml^2 molecule^{-2} sec^{-1}; T = 1400 to 1600 K). In a review of Reaction (3), Kaufman[33] suggests that the flame k's are somewhat smaller than expected for a fully allowed three-body process involving a low ionization-potential electron-donor atom and a moderately electronegative molecule. Since competitive sodium oxide/free radical (H, O and OH) reactions effectively reversing Reaction (3) can readily occur in $H_2/O_2/N_2$ flames, and are difficult to account for quantitatively, it would not be unexpected to obtain values of k_3 by the fast-flow reactor technique which are significantly higher than those observed in flames.

The present result for k_3 is considerably lower than the Polyani-diffusion flame measurement of Bawn and Evans[34] ($\approx 3 \times 10^{-30}$ ml^2 molecule^{-2} sec^{-1} at 533 K). Blamont and Donahue[35] have pointed out that the Bawn and Evans value could be as much as an order of magnitude too high due to neglect of the quenching effect of N_2 on Na(^{2}P) and of pressure broadening in the determination of the absolute Na(^{2}S) ground state concentration. Such a corrected value still would be considerably higher than suggested by the present results and those of the flame work. Fontijn[36] has noted that the diffusion flame results were obtained under conditions such that a fog of oxide particles was present and that if binary heterogeneous oxidation were rapid the results obtained could have little to do with the homogeneous Reaction (3). The present work has shown that heterogeneous oxidation is indeed rapid (at least at 1200 K), thus reinforcing this suspicion.

Conclusion

An extension of the working range of the tubular fast-flow reactor from an upper limit of 1000 K to 2000 K has been accomplished. As adapted, the fast-flow reactor technique permits studies of homogeneous and heterogeneous reaction kinetics well above the lower limit of previously used high temperature techniques (flames, shock tubes, etc.). A new method for obtaining definitive chemical kinetic data at moderately high temperatures is thus provided, offering a needed bridge between low and high temperature kinetic techniques. The first application has been to the measurement of homogeneous metal atom oxidation kinetics; relatively fast, dominant binary abstraction and ternary association reactions take place with O_2, accompanied by fast competing wall reactions.

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APPENDIX

Heterogeneous Fe-Oxidation

Interpretation of $[Fe]_{rel}$-decay profiles at 3 Torr according to the simple plug flow or parabolic flow analyses[27,28] yields a value of $(1.7 \pm 0.5) \times 10^3$ sec^{-1}, or $(2.7 \pm 0.8) \times 10^3$ sec^{-1}, for k_W, respectively. In the absence of diffusional limitations, simple kinetic theory[28] yields $k_W = (v/4)\,\gamma$ (Surface Area/Volume), where v is the mean thermal velocity of Fe atoms. Using this relation, we calculate a value for γ of 0.54×10^{-1} or 0.88×10^{-1} from the data, corresponding to the plug flow or parabolic flow interpretation, respectively. Diffusional limitations are, however, non-negligible, even at 3 Torr; thus, for pure diffusion control, $k_W = (23.2/d^2)\,D$ for plug flow[27] and $k_W = (14.6/d^2)\,D$ for parabolic flow,[27] where D is the diffusivity of Fe atoms. We estimate, following the procedures of Ref. 37, $D \approx 0.76 \times 10^3$ cm^2 sec^{-1} at 3 Torr and 1600 K, which yields $\approx 2.8 \times 10^3$ sec^{-1} and $\approx 1.7 \times 10^3$ sec^{-1} for k_W (diffusion-controlled) for plug and parabolic flow, respectively. Since the observed values of k_W are so close to the diffusion-limited values, the above reported value of $\gamma_{Fe,\,1600\,K}$ has to be considered a lower limit.

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Table I

Rate Coefficient of $Fe + O_2 \rightarrow FeO + O$ at 1600 K

λ (nm)	P (Torr)[a]	$\bar{v}$ (m sec^{-1})	$[O_2]$ (10^{15} ml^{-1})	[M] (10^{17} ml^{-1})	$\bar{T}$ (K)	k_1 (10^{-13} ml $molecule^{-1}$ sec^{-1})
248.3	15	109	0.5 to 3.6	0.91	1596	4.3
372.0	15	49	0.1 to 6.8	0.91	1593	5.1
372.0	15	111	0.5 to 6.8	0.92	1581	4.1
248.3	30	28	0.9 to 5.4	1.8	1592	3.6
248.3	30	56	0.5 to 7.0	1.8	1607	2.3
372.0	30	24	0.9 to 10.3	1.8	1608	3.7
372.0	30	24	0.2 to 5.2	1.8	1594	3.3
372.0	30	24	0.2 to 5.3	1.8	1606	3.1
248.3	45	36	0.7 to 8.1	2.7	1578	4.2
248.3	60	21	0.4 to 7.2	3.6	1590	2.8
372.0	60	24	0.2 to 7.0	3.6	1597	2.9
				Mean:	1595	3.6

[a] 1 Torr = 133.3 N m^{-2}

List of Figure Captions

Fig. 1 Schematic of apparatus.

Fig. 2 Fe-atom concentration profile. $\bar{T}$ = 1589 K; $\bar{v}$ = 48.6 m sec^{-1}; $[O_2]$ = 0.89 × 10^{15} ml^{-1}; λ = 372.0 nm; P = 15 Torr.

Fig. 3 Fe/O_2 reaction rate coefficient at 15 Torr. $\bar{T}$ = 1593 K; $\bar{v}$ = 49 m sec^{-1}; [M] = 0.91 × 10^{17} ml^{-1}; λ = 372.0 nm. Numbers beside each individual data point indicate the $\bar{T}$ at which it was obtained.

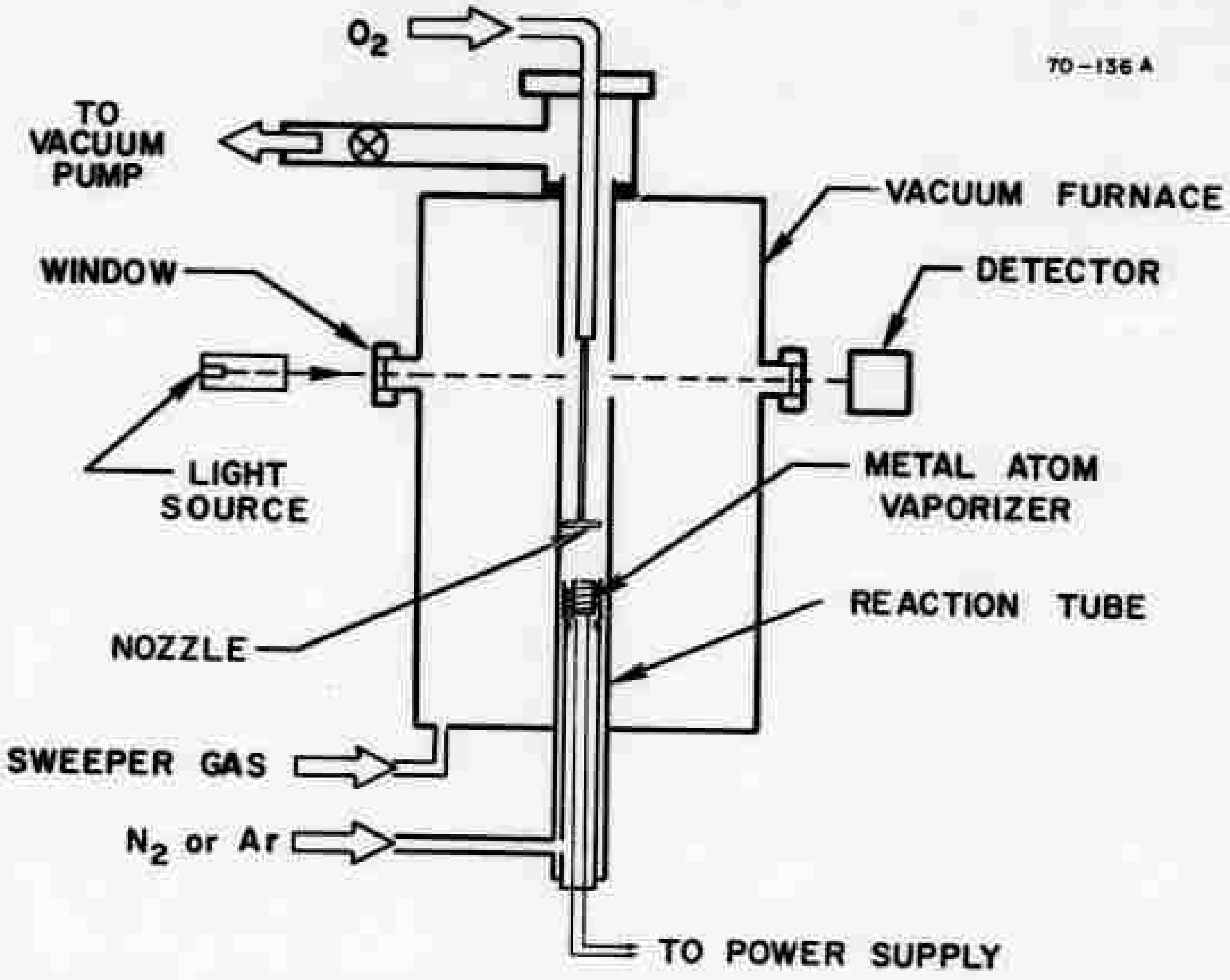
70-136 A
O_2
TO VACUUM PUMP
VACUUM FURNACE
WINDOW
DETECTOR
LIGHT SOURCE
METAL ATOM VAPORIZER
NOZZLE
REACTION TUBE
SWEEPER GAS
N_2 or Ar
TO POWER SUPPLY

Fig. 1

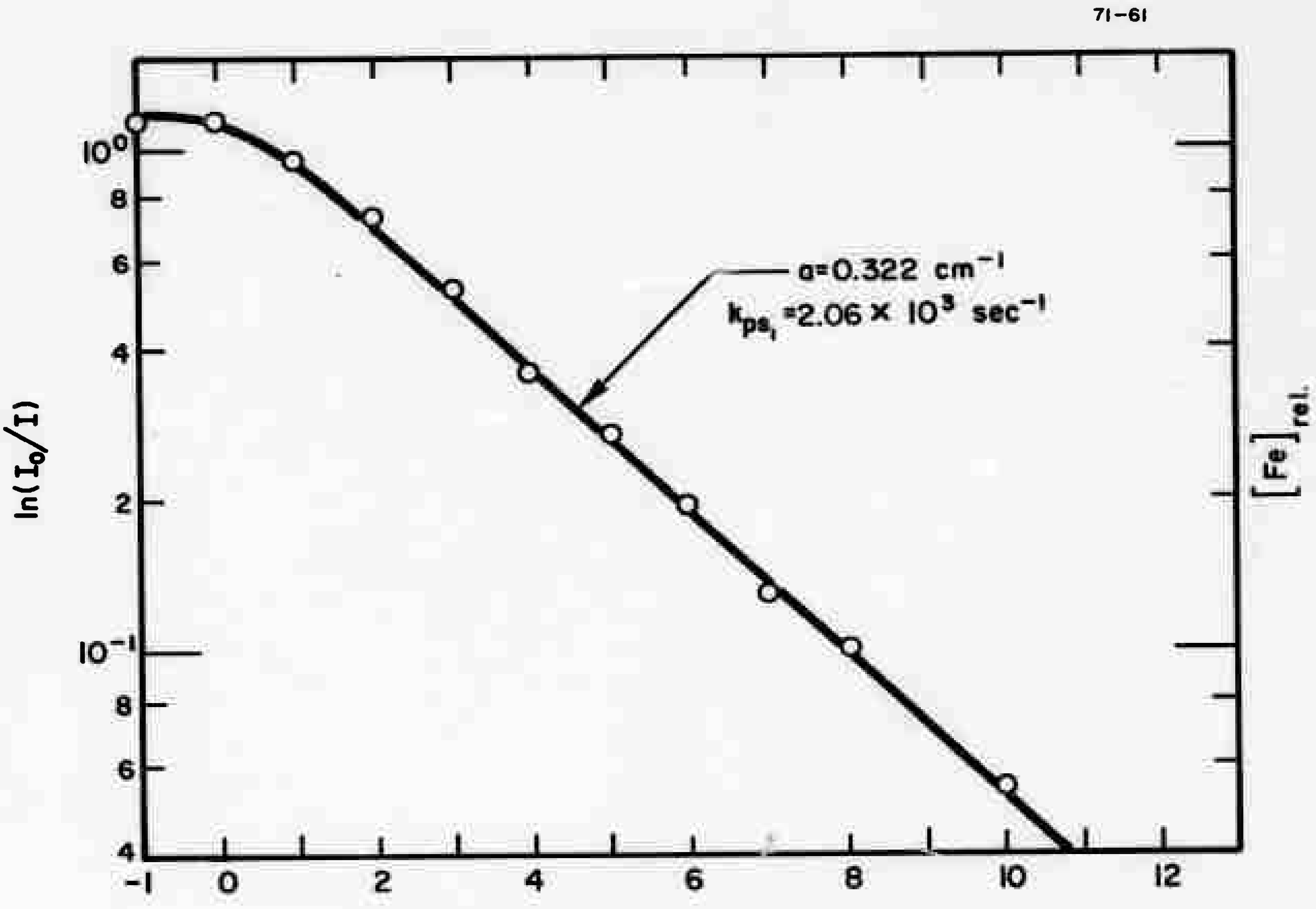
71-61
10^0
8
6
4
2
10^{-1}
8
6
4
-1
0
2
4
6
8
10
12
$\ln(I_0/I)$
$[Fe]_{rel.}$
$a = 0.322\ cm^{-1}$
$k_{ps_1} = 2.06 \times 10^3\ sec^{-1}$
DISTANCE O_2 INLET TO PORT, cm

Fig. 2

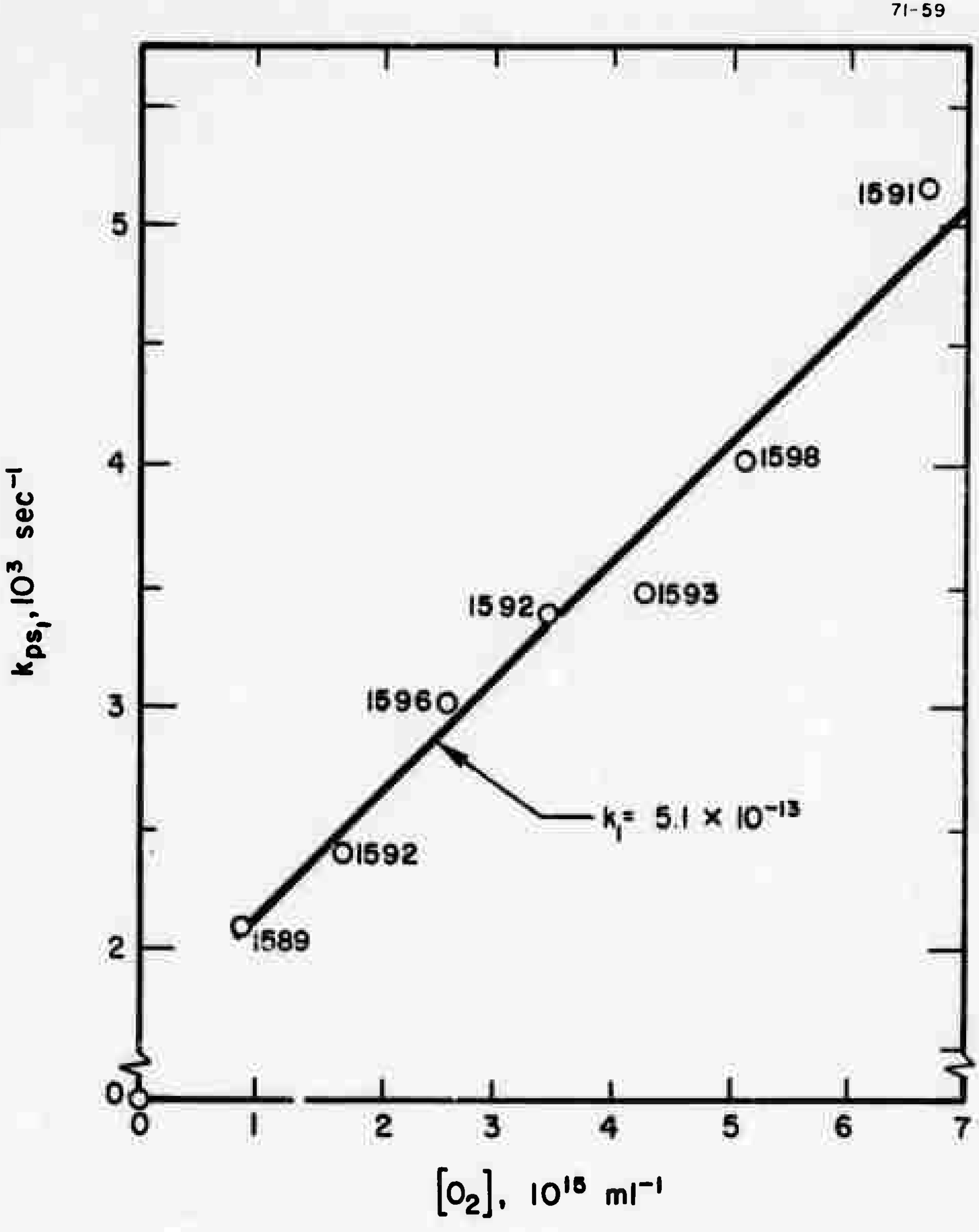
71-59
k_{ps_1}, 10^3 sec^{-1}
0
2
3
4
5
0
1
2
3
4
5
6
7
$[O_2]$, 10^{15} ml^{-1}
1589
1592
1596
1592
1593
1598
1591
$k_1 = 5.1 \times 10^{-13}$

Fig. 3

APPENDIX C

TUBULAR FAST-FLOW REACTOR STUDIES AT HIGH TEMPERATURES. I. KINETICS OF THE Fe/O_2 REACTION AT 1600 K

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TUBULAR FAST-FLOW REACTOR STUDIES AT HIGH TEMPERATURES. 1. KINETICS OF THE Fe/O_2 REACTION AT 1600°K

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The homogeneous gas phase reaction between Fe and O_2 has been studied in an N_2 bath at 1600°K using an alumina fast-flow reactor contained in a vacuum furnace. The reaction proceeds via $Fe + O_2 \rightarrow FeO + O$ with a rate coefficient of $(3.6 \pm 1.4) \times 10^{-13}$ ml molecule^{-1} sec^{-1}. Evidence has also been obtained for a wall oxidation reaction, for which $\gamma_{Fe} \geq 10^{-1}$.

1. Introduction

The conventional cylindrical fast-flow reactor technique has made possible measurement of the kinetics of a large number of atom and free radical reactions in the 200–1000°K range. For refractory species and for determination of the temperature dependence of rate coefficients above 1000°K other, often less accurate, techniques had to be used. We have now constructed a tubular flow reactor suitable for studies up to ≈ 2000°K. The first study with the reactor concerns the reaction

$$Fe + O_2 \rightarrow FeO + O \qquad (1)$$

at 1600°K.

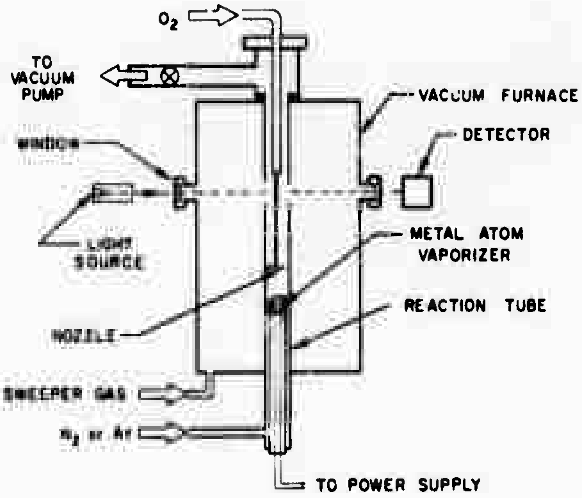

Fig. 1. Schematic of apparatus.

2. Experimental

A detailed description of the apparatus and its operation is given elsewhere [1]; a simplified drawing is shown in fig. 1. The 2.5 cm i.d. alumina reactor is contained inside a 25 cm i.d., 95 cm long, vacuum chamber. A 5.1 cm o.d. alumina muffle tube (not shown) surrounds the reactor and is wound with Pt–40% Rh resistance wire. Bath gas (N_2) passes through the reactor and entrains atomic Fe vapor from an internally resistively-heated Fe sleeve. O_2 is introduced from the downstream end of the apparatus through a multi-hole ring-shaped Pt–10% Rh nozzle located at the end of a movable alumina tube. The reaction time is proportional to the distance from this nozzle to the observation port and is varied by changing the nozzle position. Relative Fe-concentrations in the gas arriving at the observation port are measured by absorption of the chopped 248.3 or 372.0 nm Fe I emission line from an Ne-filled Westinghouse hollow-cathode lamp; $[Fe]_{rel} \propto \ln(I_0/I)$.

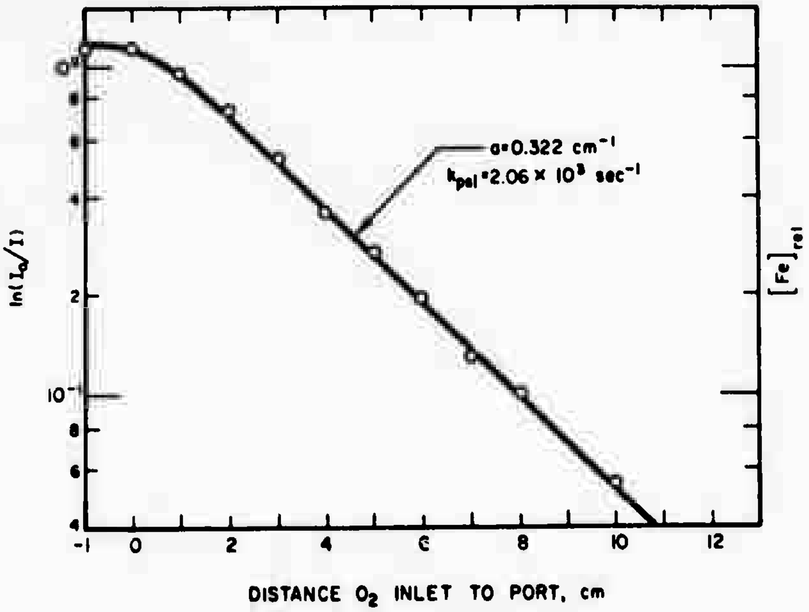

Fig. 2. Fe-atom concentration profile. $\overline{T} = 1589^\circ$K; $\bar{v} = 48.6$ m sec^{-1}; [O$_2$] = 0.89×10^{15} ml^{-1}; $\lambda = 372.0$ nm; $p = 15$ torr.

In order not to interfere with these optical measurements, the O_2 inlet tube is offset 0.6 cm laterally from the reactor axis.

To permit taking a rapid approximate scan of the reactor temperature profile, five thermocouples are situated at fixed axial stations on the outside wall of the reactor. The temperature of the reactor gas stream is measured by a 0.025 cm diam Pt/Pt–10% Rh thermocouple adjacent to the movable O_2 inlet and is ≈ 20°K lower than at the corresponding fixed stations. Temperature at each fixed station remains constant to within ± 5°K during experiments; temperature differences along the ≈ 30 cm useful length of the reaction tube axis are ≈ ± 25°K. A stronger temperature drop occurs close to the observation port, which acts effectively as a heat sink in a radiant enclosure. In addition to flow disturbances near the ports (see below), this is a reason to reject the data obtained close to the ports. $\overline{T}$ is taken as the integrated mean of the centerline thermocouple readings over the linear region of the data plots, see fig. 2. $\overline{T}$ is reproducible within ± 10°K from run to run (cf. fig. 3).

Pressure measurement stations are located upstream and downstream of the reactor. Over the range of conditions investigated, table 1, no pressure drop (i.e., $\Delta p < 0.2$ torr) along the length of the reactor is

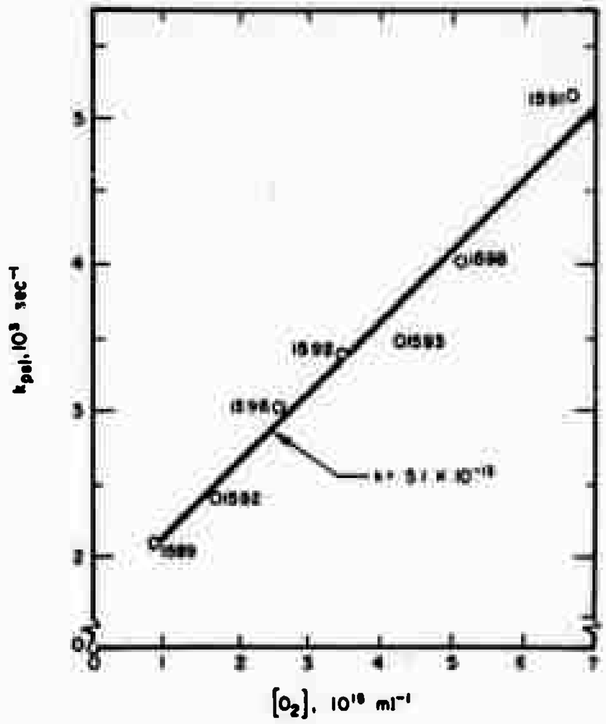

Fig. 3. Fe/O$_2$ reaction rate coefficient at 15 torr. $\overline{T} = 1593^\circ$K; $\bar{v} = 49$ m sec^{-1}; [M] = 0.91×10^{17} ml^{-1}; $\lambda = 372.0$ nm. Numbers beside each individual data point indicate the $\overline{T}$ at which it was obtained.

Table 1
Rate coefficient of $Fe + O_2 \rightarrow FeO + O$ at 1600°K

λ (nm)	p (torr) [a]	$\bar{v}$ (m sec^{-1})	$[O_2]$ (10^{15} ml^{-1})	[M] (10^{17} ml^{-1})	$\bar{T}$ (°K)	k (10^{-13} ml molecule^{-1} sec^{-1})
248.3	15	109	0.5 to 3.6	0.91	1596	4.3
372.0	15	49	0.1 to 6.8	0.91	1593	5.1
372.0	15	111	0.5 to 6.8	0.92	1581	4.1
248.3	30	28	0.9 to 5.4	1.8	1592	3.6
248.3	30	56	0.5 to 7.0	1.8	1607	2.3
372.0	30	24	0.9 to 10.3	1.8	1608	3.7
372.0	30	24	0.2 to 5.2	1.8	1594	3.3
372.0	30	24	0.2 to 5.3	1.8	1606	3.1
248.3	45	36	0.7 to 8.1	2.7	1578	4.2
248.3	60	21	0.4 to 7.2	3.6	1590	2.8
372.0	60	24	0.2 to 7.0	3.6	1597	2.9
				Mean:	1595	3.6

[a] 1 torr = 133.3 N m^{-2}.

observed. Routine [2] gas handling procedures are used. Nitrogen is obtained directly from a liquid N_2 container. Linde U.S.P. O_2 is dried by passage over activated alumina. Ar was used as the bath gas in a few experiments in which it was established that N_2 does not react with Fe at a measurable rate.

To prevent the reaction gases from entering the vacuum jacket through the reaction tube ports, an N_2 sweeper gas volume flow rate of about one tenth that of the reaction tube flow rate is passed through the furnace. The flow of sweeper gas into the reactor at the observation ports does not, however, interfere with our ability to make metal atom oxidation rate measurements, since these measurements are based on the change in reactant concentration as a function of reaction time when the O_2 nozzle is moved between points well upstream from the observation point. The validity of operating in this manner has been demonstrated by other workers [3,4] concerned about having the measurement station at a point downstream from the useful observation zone at different reaction conditions.

The pseudo-first order rate interpretation used here implicitly requires $[O_2] \gg [Fe]$. The fractional emission line absorption varied from as high as $\approx 90\%$ at the upstream end of the reaction zone to $\approx 1\%$ at the detection threshold. Using recent estimates by Linevsky [5] these figures correspond to 6×10^{12} ml^{-1} > [Fe] > 1×10^{10} ml^{-1}, well below the O_2 concentrations used (table 1).

3. Results

Fig. 2 shows a typical first order data plot. The pseudo-first order rate coefficient k_{ps_1} has been obtained from the local slope $a = -\mathrm{d} \ln [Fe]/\mathrm{d}x$ of these plots via the equation $k_{ps_1} = \eta a \bar{v}(1 + aD_{Fe}/\bar{v})$, in which η is a factor equal to 1 for plug flow and approximately equal to 1.6 for parabolic flow [6]; $\bar{v}$ is the mean bulk linear gas velocity; D_{Fe} is the diffusivity of Fe atoms; $(1 + aD_{Fe}/\bar{v})$ is the correction factor for the effects of axial diffusion [7], which yields a less than 10% change in the rate coefficients for the conditions of table 1. For our calculations we have taken η to be 1.3 ($\pm$ 0.3).

The k_{ps_1} values thus calculated from the data have been plotted against $[O_2]$, cf. fig. 3, to yield k, the second-order rate coefficient. The k-data thus obtained have been assembled in table 1. They are independent of [M], demonstrating that the predominant Fe oxidation path is reaction (1). The normalized standard deviation of the determination of k is 22%. Allowing for a possible $\approx 20\%$ systematic error and the 23% uncertainty in η, the total uncertainty in k is $\approx 40\%$, hence the measured rate coefficient for reaction (1) is $(3.6 \pm 1.4) \times 10^{-13}$ ml molecule^{-1} sec^{-1}.

The initial experiments were made at a pressure of 3 torr. Upon O_2 addition rapid Fe consumption is observed. The rate is of first ord [Fe] and of zeroth order in $[O_2]$ over the range

$1 \times 10^{12} < [O_2] < 2 \times 10^{13}$ ml^{-1}, indicative of a heterogeneous oxidation process. From these experiments the lower limit for the oxidation probability per Fe atom collision with the wall, $\gamma_{1600°K}$, is referred to be on the order of 1×10^{-1}. To definitively determine this number, work at appreciably lower pressures would be required to remove diffusional transport limitations complicating the measurements of γ at 3 torr. At the higher pressures, where the homogeneous reaction could be measured, the contribution of the wall reaction is evident in the positive intercept of the k_{ps_1} versus $[O_2]$ plots, cf. fig. 3.

4. Discussion

While the temperature dependence of k has not yet been determined we may for the present assume the activation energy to be approximately equal to the estimated [8, 9] endothermicity of reaction (1), 20 kcal mole^{-1}. The above results then correspond to $k(T) = 2.0 \times 10^{-10} \exp(-20\,000/RT)$. This pre-exponential factor is within a factor of 2 to 3 of the collision frequency rate factor, which makes it unlikely that the activation energy can be appreciably greater than 20 kcal mole^{-1}.

There have been two other attempts at measuring k. Von Rosenberg and Wray [10] found in shock tube work at temperatures at 2400°K and greater that the reaction was too fast to measure, and set an approximate limit $k(2400°K) \geq 5 \times 10^{-12}$ ml molecule^{-1} sec^{-1}, in good agreement with the above $k(T)$ value which yields 3×10^{-12} ml molecule^{-1} sec^{-1} at 2400°K. Linevsky [5], working in lean CO/H_2/air flames at 1500°K, found that due to the rapidity of the exothermic back reaction (−1), an Fe concentration near equilibrium is established, and concluded that $k(1500°K) \geq 10^{-14}$ ml molecule^{-1} sec^{-1}, also consistent with the present result.

Acknowledgements

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