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COMBUSTION KINETICS OF METAL OXIDE AND HALIDE RADICALS

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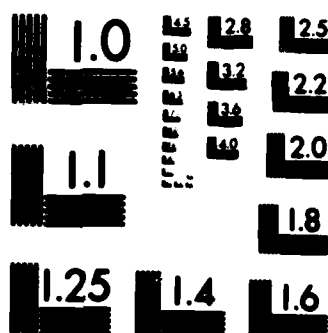
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10 to the -14th power

$\rightarrow$ equals $2 \times 10^{-14} \exp(530/T)$ ~~cm~~ molecule⁻¹ s⁻¹. The reaction thus has a slight negative temperature dependence. It is concluded that the O-(A10) bond formed has an energy equal to or exceeding 530 kJ/mol⁻¹, much larger than reported in the literature. A possible reason for this disagreement is discussed. Originator supplied keywords include:

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MATTHEW J. KURPIER

Chief, Technical Information Division

I. RESEARCH OBJECTIVES

Current ability to improve the combustion efficiency of metalized propellants is severely hampered by a lack of understanding, and knowledge, of the ways and manner by which temperature affects the rate coefficients of individual reactions and reaction channels. While the simple Arrhenius-type equation $k(T) = AT^{1/2} \exp(-E_A/RT)$ has over limited temperature ranges been of great value, when applied to wide temperature ranges it is often not obeyed. Particularly for exothermic and slightly endothermic reactions, order of magnitude errors can be made by extrapolations based on the Arrhenius equation¹. It is the goal of the present program to provide an insight in the kinetic behavior of metallic radical oxidation reactions as influenced by temperature.

Figure 1 shows the reactions of interest and their relevance to advanced propulsion systems development. It also gives a schematic of the HTFFR, high-temperature fast-flow reactor, method we are using to generate the metallic radicals and measure their oxidation kinetics. This unique tool, suitable for the 300 - 1900 K temperature range, provides measurements on isolated elementary reactions in a heat bath. With traditional high temperature techniques, such as flames and shock tubes, such isolation is usually impossible to achieve; as a result, data on any given reaction depend on the knowledge of other reactions occurring simultaneously, leading to large uncertainties.

The ultimate results of our work with this apparatus are to be:

- (1) Wide T-range $k(T)$ expressions for each of a number of metallic radical oxidation reactions, and

HIGH TEMPERATURE COMBUSTION KINETICS OF METALS

SCIENTIFIC APPROACH

GOALS

- UNDERSTAND THE MECHANISMS OF METALLIC RADICAL OXIDATION REACTIONS.
- MEASURE REACTION RATE COEFFICIENTS FOR REACTIONS IMPORTANT TO ADVANCED PROPULSION SYSTEMS:
 - $\text{BCl} + \text{O}_2 \longrightarrow$ Emissions from Air Breathing Missile Plume After Burning
 - $\text{AlO} + \text{CO}_2 \longrightarrow$ Combustion of Aluminized Composite Propellants
 - $\text{BO} + \text{O}_2 \longrightarrow$ Combustion of Boron Slurries
 - $\text{AlCl} + \text{O}_2 \longrightarrow$ Microparticulates Formation
 - $\text{AlF} + \text{O}_2 \longrightarrow$ Tendency of Fluorinated Binders to Reduce Agglomeration
- OBTAIN THESE $k(T)$ DATA OVER THE 300–2,000 K RANGE. NON-ARRHENIUS BEHAVIOR PRECLUDES EXTRAPOLATION FROM NARROW TEMPERATURE INTERVALS.

TECHNIQUE

High-Temperature Fast-Flow Reactor

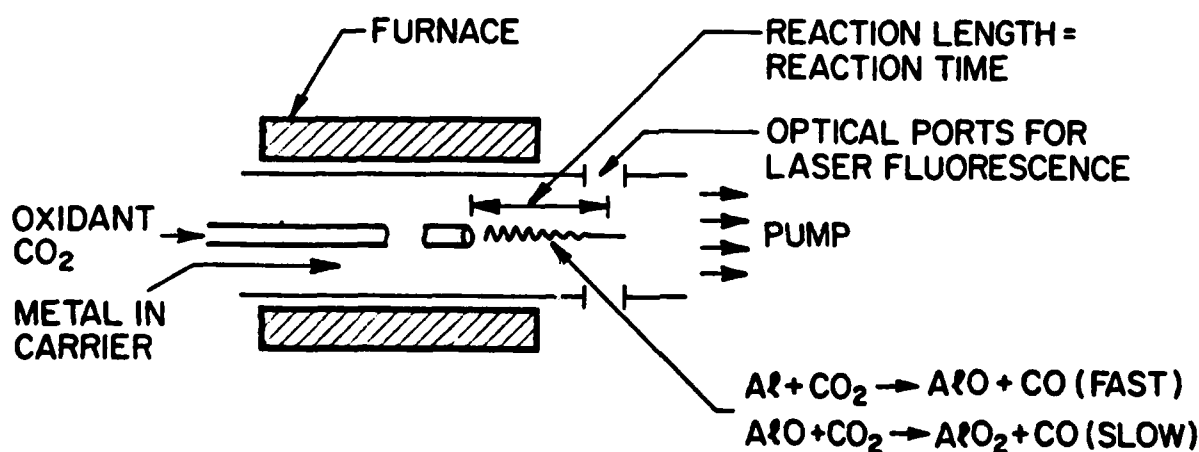
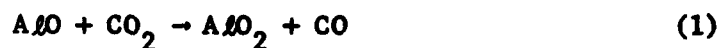


Figure 1

- (11) Based on (1), an improved understanding of the chemistry which governs the temperature dependence of such reactions.

II. STATUS OF THE RESEARCH EFFORT

Our efforts during the reporting period have concentrated on the reaction



A brief report on the results from 450 to 1300 K has been issued² and a paper fully describing the completed study is in preparation.

Initial experiments showed that above about 450 K the reaction



was sufficiently fast compared to reaction (1) that it could be used as the source of AlO. The production and reaction of AlO following this approach is illustrated in Figure 1. The relative AlO concentrations were measured by laser-induced fluorescence (LIF) as illustrated by Figure 2. The measured rate coefficients from 100 experiments, covering the 450 to 1300 K range, are shown in Figure 3. These results are independent of pressure from 1 to 5 kPa and flow velocity from 30 to 170 m s⁻¹. Analysis of the data using the propagation of errors treatment and data weighting methods, described previously³, resulted in:

$$k_1(T) = (2.2 \pm 1.2) \times 10^{-14} \exp[(529 \pm 322)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

In this expression the error limits in the exponential are two standard deviations while those in the pre-exponential are two standard deviations

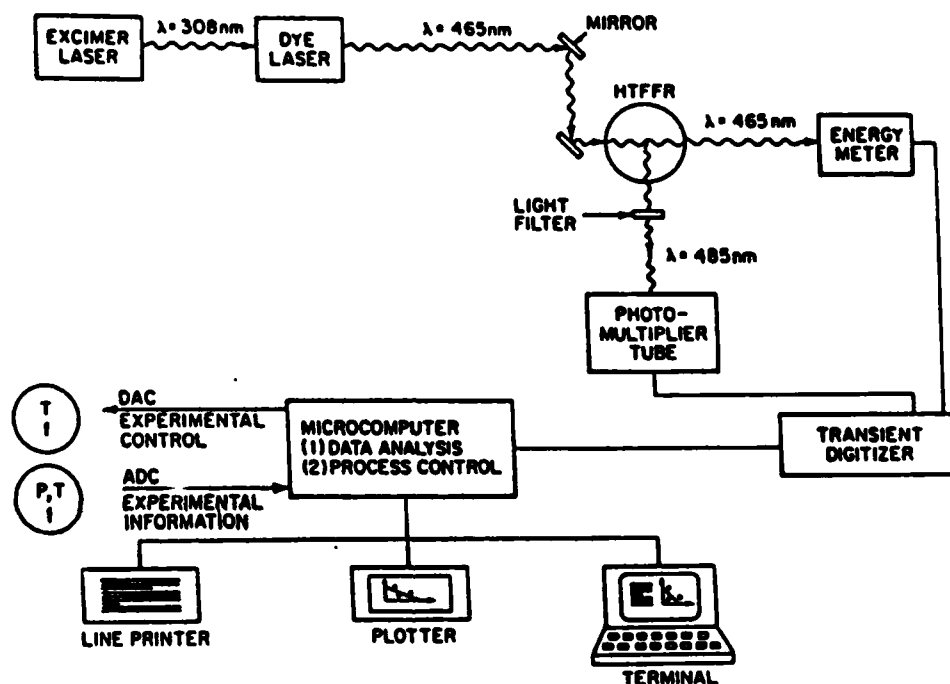


Figure 2 Experimental Arrangement for the Study of A/O Radical Reactions Using Laser-Induced Fluorescence

~~~~~ Radiation; ————— Electrical Connections

T = Temperature; f = Volume Flow Rate; P = Pressure;  
 DAC = Digital to Analog Converter; ADC = Analog to Digital Converter

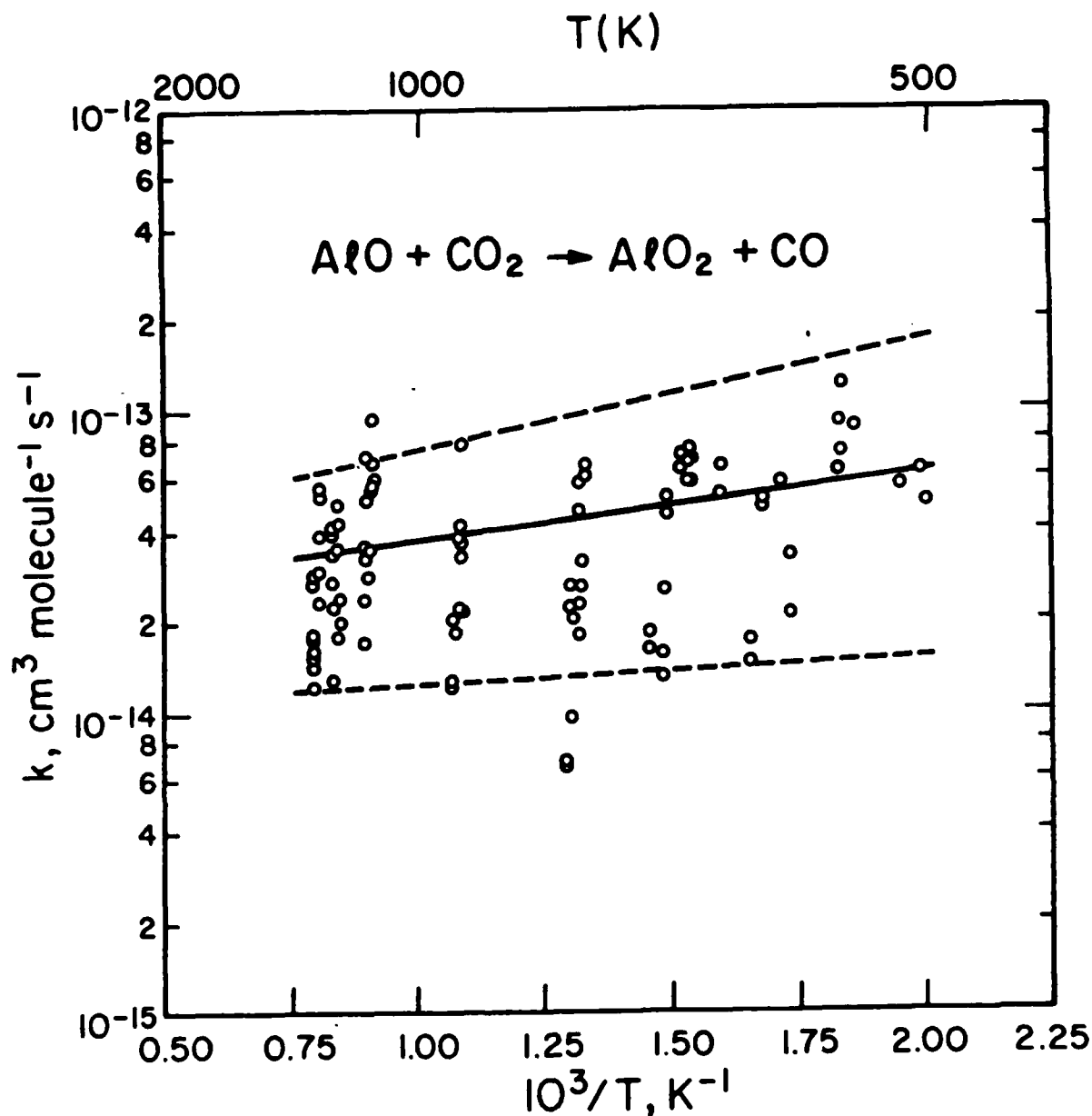


Figure 3 Arrhenius-Type Plot for the  $AlO + CO_2 \rightarrow AlO_2 + CO$  Reaction. Individual data points as measured.

————— Calculated rate expression given in the text.  
 - - - - - Error limits of the rate expression, given in the text.

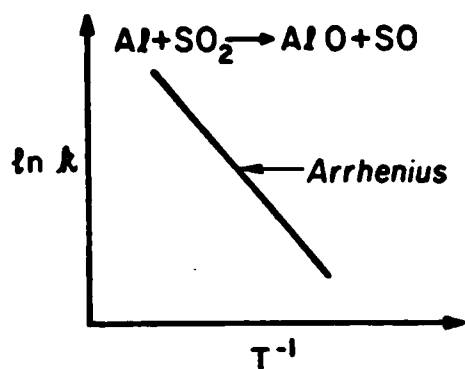
plus a 10% systematic error for the uncertainty in the flow profile factor<sup>3</sup>. The measurements have been extended to  $\approx 1500$  K, but these results (while clearly not showing any different trends) have not yet been fully analyzed.

The kinetic significance of this result, i.e., a reaction with a slight negative activation energy, can best be discussed by the comparison to the  $Al/SO_2$  and  $Al/CO_2$  reactions illustrated by Figure 4. The  $Al/SO_2$  reaction<sup>4</sup> has a normal Arrhenius  $k(T) = A \exp(-E_A/RT)$  behavior. The  $Al/CO_2$  reaction (2) has a normal (straight line  $\ln k$  vs.  $T^{-1}$ ) Arrhenius positive T-dependence from 300 - 700 K and then a much more rapidly increasing  $k$  with increasing  $T$ .<sup>5</sup> While transition state theory predicts mild upward curvature for many Arrhenius-type plots<sup>1</sup>, the behavior of reaction (2) is indicative of a second reaction channel which becomes important at higher temperatures. Specifically the very rapid increase in  $k_2$  with temperature above 700 K may be attributed to the thermal equilibrium increase in the concentration of  $CO_2$  in bending vibrational modes<sup>1,5</sup>. Contrary to ground-state linear  $CO_2$ , which has a negative electron affinity and can interact with  $Al$  only by a covalent mechanism (neutral potential surface), bent  $CO_2$  can interact at larger distances by an ionic (electron jump or harpooning) mechanism. Larger interaction distances are equivalent to larger collision cross sections and hence can lead to larger frequency factors of rate coefficients.

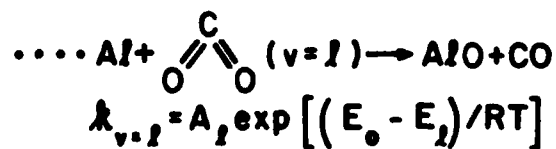
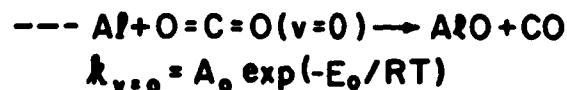
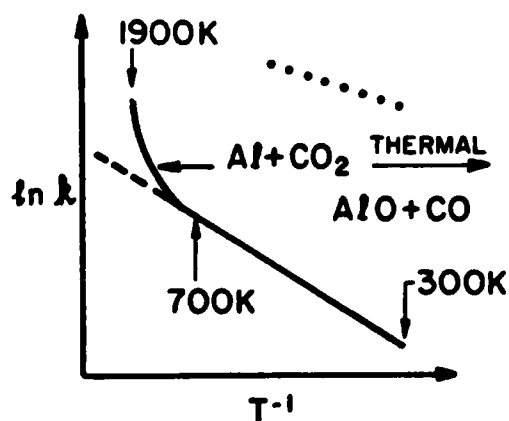
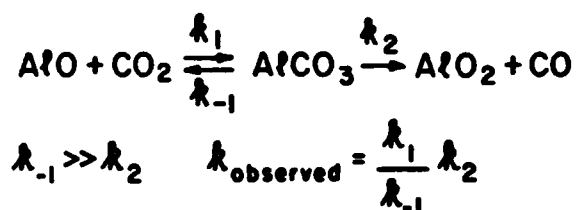
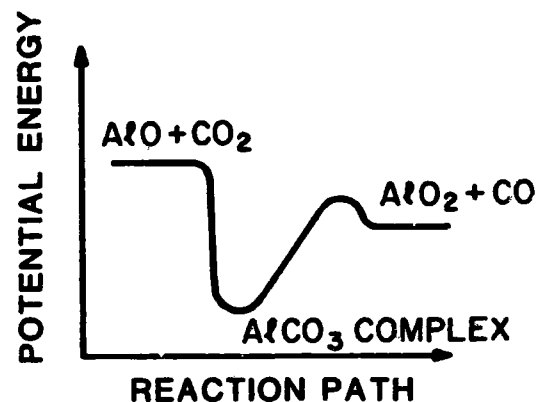
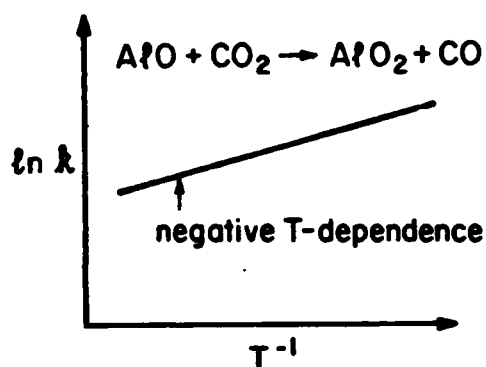
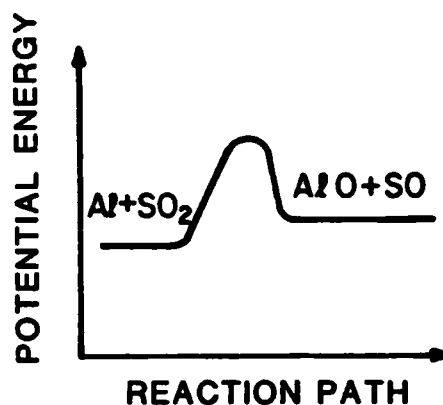
Ionic interaction distances are roughly proportional to  $[IP (\text{metallic species}) - EA (\text{oxidant})]^{-1}$ , where  $IP$  = ionization potential and  $EA$  = electron affinity. As a result ionic interactions

# ACCOMPLISHMENTS

## OBSERVATION



## INTERPRETATION



$A_1 \gg A_0$ , i.e. BENT  $\text{CO}_2$   
HAS MUCH LARGER REACTION  
CROSS SECTION THAN LINEAR  $\text{CO}_2$

Figure 4

will lead to larger interaction distances only for low ionization potential reactants such as free metal atoms, e.g.,  $IP(Al) = 5.98$  eV. By contrast  $IP(AlO) = 9.5 \pm 0.5$  eV, and assuming our explanation for the  $Al/CO_2$  reaction to be correct, no similar sharp increase with  $T$  was anticipated for reaction (1). The results of Figure 3 now confirm this. The slight negative  $T$ -dependence of reaction (1) is indicative of a reaction proceeding via an intermediate bound complex which preferentially dissociates to reactants rather than products<sup>1</sup>:



The low value of the pre-exponential of the  $k_1(T)$  expression is a further indication of such redissociation to reactants.

The negative activation energy of the  $AlO/CO_2$  reaction leads to another interesting conclusion, i.e., that the new bond formed is at least as strong as the bond being broken (otherwise the reaction has to have a positive activation energy at least equal to its endothermicity). The O-CO bond energy is  $530 \text{ kJ mol}^{-1}$  and hence the new O-(AlO) bond has to be at least this strong. While long elusive, the  $AlO_2$  molecule has recently been observed by Ho and Burns<sup>6</sup> in  $Al_2O_3$  evaporation experiments with mass spectrometric detection of products. Their heat of formation values allow only  $420 \pm 40 \text{ kJ mol}^{-1}$  for the new bond in  $AlO_2$ . It has been argued that in our HTFFR experiments only the disappearance of AlO is observed; not the appearance of  $AlO_2$ , the optical spectrum of which is unknown. However, there is no other chemically reasonable product for the pressure independent reaction (1). The assumption that the  $AlO_2$  produced by reaction (1) is not identical

to that observed from evaporation appears to be the most reasonable way to reconcile the observations. Theoretical considerations suggest  $O-Al-O$  as the most stable configuration, some  $90 \text{ kJ mol}^{-1}$  more stable than  $Al-O-O$ .<sup>7</sup> It is thus likely that the product of reaction (1) has the  $O-Al-O$  structure. It is however as yet unclear why the evaporation experiments should yield a less stable structure. Perhaps this is an experimental artifact related to the fact that  $AlO_2$  is observed to be only a minor species in those experiments, in contrast to  $Al_2O$  which they<sup>6</sup> observed as the major triatomic product. Possibly the  $O-Al-O^+$  ion is unstable and could therefore not be detected mass spectrometrically. Adding a mass spectrometer to the HTFFR might be a future means of clarifying this problem.

The reactor with which the results of Figure 3 were obtained used Kanthal A heating wire. This wire is nominally suitable for work-up to about 1500 K, though we found 1300 K to be an approximate practical upper limit. In earlier HTFFR work<sup>3-5</sup> we used Pt/Rh heating wire for temperatures up to about 1900 K. As frequent burnouts occurred with this material above  $\approx 1500 \text{ K}$ , which required laborious repairs, we decided to develop a new method to reach higher temperatures. After trial-and-error experiments in the preceding year, we built a reactor this year with easily replaceable SiC heating elements. This reactor has successfully operated at 1800 K and has been used for the above-mentioned extension of the  $AlO/CO_2$  study to 1500 K. For that reaction it is however not practical to work above 1500 K, nor do the 450 - 1500 K results indicate such to be important. The reason for this temperature limit is that the 485 nm  $AlO$  fluorescence radiation, Figure 2,

there is hard to measure, due to the radiation from the hot reactor walls. Fluorescence detection of BCl (the reaction of which with  $O_2$  we plan to study next), would be made at much shorter wavelengths (around 278 nm), where wall radiation would interfere less and consequently higher reactor temperatures can be used.

### III. CUMULATIVE LIST OF PUBLICATIONS

1. A. Fontijn and M.A.A. Clyne, Eds., Reactions of Small Transient Species. Kinetics and Energetics, Academic Press, London, 1983.
2. A. Fontijn and R. Zellner, "Influence of Temperature on Rate Coefficients of Bimolecular Reactions," in *ibid.*, Chap.1.
3. A. Fontijn, "Use of Laser-Induced Fluorescence for Fundamental Gas-Phase Kinetic Measurements," *Progress in Astronautics and Aeronautics*, 92, 147-174 (1984).
4. A. Fontijn, "Combustion Kinetics of Metal Atoms and Metallic Radicals Over Wide Temperature Ranges," 21st JANNAF Combustion Meeting (October 1984).

### IV. PROFESSIONAL PERSONNEL

Andrew J. English, following the granting of his M.E. degree based on the work performed on this grant, decided not to proceed to a Ph.D. He continued on this project until May, when he was replaced by a Ph.D. student, Donald F. Rogowski, M.Sc. Jeffrey Hyatt, an undergraduate research assistant, also has carefully assisted with the work.

## V. PRESENTATIONS AND OTHER INTERACTIONS

In the reporting period, Dr. Fontijn presented papers and seminars related to high temperature reactions of metallic species at the:

1. Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY (February 1984)
2. AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, CA (March 1984)
3. Department of Chemistry, Louisiana State University, Baton Rouge, LA (March 1984)
4. IBM Research Laboratory, San Jose, CA (May 1984)
5. AFOSR Specialists Meeting on Boron Combustion, Pittsburgh, PA (June 1984)
6. 21st JANNAF Combustion Meeting, Laurel, MD (October 1984).

Mr. Rogowski presented our paper at the Clearwater Beach Meeting of the Eastern Section of the Combustion Institute in December 1984.

Dr. Fontijn had intensive discussions on aluminum combustion problems with Dr. D.P. Weaver (AFRPL) during the above-mentioned AFOSR Contractors and JANNAF meetings. Similarly, in-depth discussions with Air Force and contractor personnel took place during the Boron Combustion Specialists Meeting. Dr. Kizirnis of AFWL Wright-Patterson Air Force Base contacted us to obtain information on the status of boron combustion diagnostics.

VI. REFERENCES

1. A. Fontijn and R. Zellner, "Influence of Temperature on Rate Coefficients of Bimolecular Reactions," Reactions of Small Transient Species. Kinetics and Energetics, A. Fontijn and M.A.A. Clyne, Eds. (Academic Press, London, 1983), Chap.1.
2. D.F. Rogowski, A.J. English and A. Fontijn, "An HTFFR Kinetics Study of the Reaction  $AlO + CO_2 \rightarrow AlO_2 + CO$ ," Eastern Section, The Combustion Institute, December 1984 Meeting, Clearwater Beach, Florida, Paper 83.
3. A. Fontijn and W. Felder, "High Temperature Flow Tubes. Generation and Measurement of Refractory Species," in Reactive Intermediate in the Gas Phase. Generation and Monitoring, (D.W. Setser, Ed.), Academic Press, New York, 1979, Chap.2.
4. A. Fontijn and W. Felder, "HTFFR Kinetics Studies of the  $Al/SO_2$  Reaction from 700 - 1600 K. Implications for  $D(Al-O)$ ," J. Chem. Phys. 71, 4854 (1979).
5. A. Fontijn and W. Felder, "HTFFR Kinetics Studied of  $Al + CO_2 \rightarrow AlO + CO$  from 300 to 1900 K, a Non-Arrhenius Reaction," J. Chem. Phys. 67, 1561 (1977).
6. P. Ho and R.P. Burns, "A Mass Spectrometric Study of the  $AlO_2$  Molecule," High Temp. Sci. 12, 31 (1980).
7. A.G. Turner (1982), as quoted in JANAF Thermochemical Tables, Data Sheet on  $AlO_2$  Ideal Gas.

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