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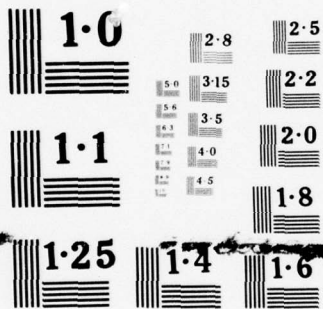
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PROJECT SQUID

TECHNICAL REPORT AC-16-PU

HTFFR KINETICS STUDIES OF $A1 + CO_2 \rightarrow A1O + CO$ FROM 300 to 1800 K, A NON-ARRHENIUS REACTION

BY

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Project SQUID is a cooperative program of basic research relating to Jet Propulsion. It is sponsored by the Office of Naval Research and is administered by Purdue University through Contract N00014-75-C1143, NR-098-038.

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Technical Report AC-16-PU

PROJECT SQUID

A COOPERATIVE PROGRAM OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

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AeroChem Research Laboratories, Inc.
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15 NPP 14-75-C-1143

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HTFFR kinetics studies of $\text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO}$
 from 300 to 1800 K, a non-Arrhenius reaction*

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High-temperature fast-flow reactors (HTFFR) were used to obtain the rate coefficients, k_1 (and their accuracies), for the reaction $\text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO}$. At 310, 480, 730, 1470, and 1830 K, k_1 is found to be $(1.5 \pm 0.6) \times 10^{-13}$, $(6.9 \pm 2.7) \times 10^{-13}$, $(1.6 \pm 0.7) \times 10^{-12}$, $(9.0 \pm 3.8) \times 10^{-12}$ and $(3.8 \pm 1.5) \times 10^{-11}$, respectively (all in $\text{ml molecule}^{-1} \text{ s}^{-1}$ units). For this temperature range $k_1(T)$ may be expressed by the curve fitting equation

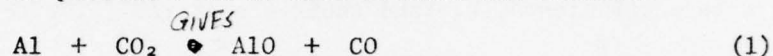
$$k_1(T) = 2.5 \times 10^{-13} T^{1/2} \exp(-1030/T) + 1.4 \times 10^{-9} T^{1/2} \exp(-14,000/T)$$

The data also indicate a wall-oxidation process of zeroth order in $[\text{CO}_2]$ with a γ_{Al} of 10^{-3} to 10^{-2} , not measurably dependent on T. Factors affecting the accuracy of the measurements are discussed. Over the 310-730 K range $k_1(T)$ obeys an Arrhenius expression, with an activation energy of $2.6 \pm 1.3 \text{ kcal mole}^{-1}$, which implies $D(\text{Al-O}) \geq 122 \text{ kcal mole}^{-1}$. Above 730 K, $k_1(T)$ increases much more rapidly with T. This behavior cannot be described on the basis of simple transition state theory alone; the most probable additional factors involved are the opening of a second reaction channel leading to $\text{AlO}(A^2\Pi)$ and preferential reaction of Al with CO_2 in bending modes.

* Prepared for submission to the Journal of Chemical Physics

I. INTRODUCTION

~~We have~~ ^{THE} previously described metal atom oxidation studies using a high-temperature fast-flow reactor (HTFFR) which, in its various modifications, allows the measurement of rate coefficients of reactions over roughly the 300-2000 K temperature range. ^{THE} ~~Our~~ earlier HTFFR measurements covered most of this range for the Al/O_2 ~~and~~ AlO/O_2 reactions. The rate coefficients of both these reactions were found to be, within experimental error, temperature independent.² In the present work we have studied the reaction



This reaction was selected since, on the basis of the most commonly accepted bond energy of AlO, it is endothermic (by about 5 to 6 kcal mole⁻¹)^{4,5} and hence has an activation energy, i.e., a temperature-dependent rate coefficient. The reaction has indeed been found here to have a positive activation energy, though evidence is discussed suggesting it may be somewhat more energetic than usually assumed.

II. TECHNIQUE

The HTFFR used in the experiments at $T \geq 730$ K was the 95 cm long single furnace unit previously described^{2,3,6} and hereafter referred to as "Reactor 1". Lower temperature experiments with Al necessitated a somewhat different design, since the heat generated by the source at the required Al fluxes is sufficient to generate a reaction zone temperature of ≈ 700 K even when no additional heat is supplied to this zone by the furnace resistance wire. The 300 K modification "Reactor 2", consisting of a high-temperature Al-atom source section and a water-cooled reaction zone, has recently been described.¹ The present work includes experiments at ≈ 480 K for which another modification of the HTFFR, shown schematically in Fig. 1,

had to be developed ("Reactor 3"). (This new reactor was also used for a few consistency checks at 730 K.) The first section of this modular HTFFR consists of a 27 cm long heated (to about 1700 K) source tube in which the Al in Ar "source gas" is generated. As in Reactor 2, this section is followed by a short (≈ 5 cm) non-insulated copper section where additional room-temperature Ar ("main gas") may be introduced. The Al/Ar flow emanates from this section at $T \approx 400$ K and flows into the independently heated reaction tube section. In this section, constructed similarly to the source section, the oxidant CO_2 is introduced through an axially traversable inlet and the relative Al concentration $[\text{Al}]_{\text{rel}}$ is measured at the observation plane (containing four windows each at 90° from the adjacent windows), using the same arrangements as in the HTFFR versions previously described.^{1-3,6} The 20 cm length of the alumina reaction tube to the observation windows can be traversed with the CO_2 inlet.

The source, main and sweeper gas, Fig. 1, was Ar obtained from high purity (99.998% min.) liquid Ar containers. Al was evaporated from Al-wetted tungsten wire sources.² Two sources of CO_2 were used: for the slower rates and shorter reaction times, predominantly a "100%" CO_2 cylinder (analyzed to contain 79 ppm O_2 and 80 ppm N_2),⁷ and (especially needed because of the increased rate coefficient, at the highest temperatures) a 9.56% CO_2 in Ar cylinder, containing < 2 ppm O_2 and < 4 ppm N_2 .⁷

Except at 1830 K, the measurements were made under pseudo first-order conditions, $[\text{CO}_2] \gg [\text{Al}]$, the basic measurement being that of $[\text{Al}]_{\text{rel}} = [\text{Al}]/[\text{Al}]_i$ as a function of $[\text{CO}_2]$, $[\text{M}]$, t and T . Here $[\text{Al}]_i$ denotes initial Al concentration in the absence of CO_2 , and $[\text{Al}]$, the Al concentration at

the observation port after CO₂ addition.^{1,2} Either fluorescence or absorption was used to measure [Al]_{rel}, using the line radiation from an Al hollow cathode lamp, chopped at 140 Hz. Additionally, prior to CO₂ introduction in each fluorescence experiment, [Al]_i was measured in absorption; thus absorption serves to determine the degree of variation in [Al]_i over all experiments. Al absorption for fluorescence measurements varied from about 3 to 20% (which is in the linear portion of the curve-of-growth); wider variation was obtained where possible by including fluorescence and absorption experiments in the set of measurements at a given temperature; for the latter an initial absorption on the order of 50% was used. Also to allow measurement of as large a variation in [Al]_i as possible, three Al lines of different oscillator strength (309.3 nm, gf = 0.70; 394.4 nm, gf = 0.23 and 396.2 nm, gf = 0.46)⁸⁻¹⁰ were used in the absorption experiments. From these gf values, a lamp temperature of 600 K¹¹ and P = 15 Torr and, assuming Doppler and pressure broadened absorption lines, [Al] is estimated to be 0.9, 1.9 and 1.0 × 10¹² ml⁻¹ at 1830 K and 1.0, 1.4 and 1.2 × 10¹² ml⁻¹ at 310 K for 50% absorption at these wavelengths, respectively. In absorption experiments the detector consisted of monochromator/PMT combinations, while for the fluorescence measurements the 309.3 nm line was used with a PMT equipped with a 309.1 nm (11 nm fwhm) interference filter as detector. Above ≈ 1500 K absorption was found to be the only practical technique because of the high background radiation from the reaction tube walls. Near 300 K only fluorescence could be used since the source conditions required for the large [Al]_i of absorption experiments led to an increase in the reaction tube temperature above that used in the fluorescence experiments.

As before^{2,3} data were obtained using either the traversing oxidant inlet mode (where measured pseudo first-order rate coefficients k_{ps_1} give the reaction rate coefficient k_1 from the slope of plots of k_{ps_1} vs. $[CO_2]$) or the stationary CO_2 inlet mode, which is more facile especially at the higher temperatures. In the latter mode k_1 is obtained directly from plots of $[Al]_{rel}$ vs. $[CO_2]$ for a given inlet position and the measurements are typically repeated at one or two additional positions (including e.g., 20, 12 and 7 cm upstream from the observation ports); the results reported from these stationary inlet measurements are the averages of two or, more commonly, three such experiments. The individual k_1 measurement plots obtained are of similar quality as those of the Al/O_2 work^{1,2} (standard deviations of 10 to 20%).

For the k_1 measurements at 1830 K the full bimolecular rate equation had to be used rather than its pseudo first-order approximation,¹² since at the lower part of the $[CO_2]$ range used, $[Al] \approx [CO_2]$. This is due to (i) the large value of k_1 (1830 K) which requires low $[CO_2]$ in order to maintain reasonable reaction rates and (ii) the high $[Al]$ inherent in the use of absorption relative to fluorescence measurements.

III. RESULTS

A. $k_1(T)$ measurements

The k_1 measurements made are summarized in Table I. It may be seen that the data at each of the five nominal temperatures used cover a wide range in pressure, P , average gas velocity, \bar{v} , and $[Al]_i$ and are independent of these quantities. In Fig. 2 the mean k_1 and standard deviation for each of these temperatures are plotted in the standard Arrhenius fashion, showing a strong departure from linearity above 730 K with an activation energy

increasing with T. To establish an analytical description of this temperature dependence least squares fits to several functional expressions for $k_1(T)$ were tried. The procedure followed was similar to that followed by Bemand, Clyne and Watson¹³ and consisted of assigning equal weights to all of the 62 data points of Table I and fitting these to expressions (A)-(D) below. The polynomials (A)-(C) were fit to successively higher degrees from 1 up to $p = 4$, $q = 4$, and $r = 3$, respectively, using linear multiple regression techniques,¹⁴ while expression (D) was fit using Marquardt's method¹⁴ for $s = 0$ and $1/2$:

$$\left. \begin{aligned} \ln k_1(T) &= \ln A_0 + A_p/T^p && \text{Arrhenius form} && \text{(A)} \\ \ln k_1(T) &= \ln A'_0 + 0.5(\ln T) + A'_p/T^p && && \text{(A')} \end{aligned} \right\}$$

$$\ln k_1(T) = \ln B_0 + B_q (\ln T)^q \quad T^n \text{ form} \quad \text{(B)}$$

$$\ln k_1(T) = \ln C_0 + C_1 (\ln T) + C_r/T^r \quad \text{Transition state theory form} \quad \text{(C)}$$

$$k_1(T) = D T^s \exp(-E/T) + F T^s \exp(-G/T) \quad \text{Double exponential form} \quad \text{(D)}$$

At each increase of p , q , and r above zero, the computed fit was examined using the F-test for significance.¹⁴ Comparisons among the various fits were made using the computed value of χ^2 such that the best fit was determined as that functional form which yielded the smallest χ^2 value. The best overall fit (minimum χ^2 value) was obtained from expression (D) with $s = 1/2$, while for each of the polynomials, (A)-(C), the maximum significant degree (F-test) was $p = q = r = 1$. Standard deviations, based on random errors only (see Sec. III.C for discussion of systematic errors) were then determined for the computed fitting expressions. The following results were obtained from (A) through (D), respectively, for the temperature dependence of k_1 (fitting error limits = 2σ):

$$\ln k_1(T) = (-24.03 \pm 0.39) - (1830 \pm 170)/T \quad (E)$$

$$\chi^2 = 0.373$$

$$\ln k_1(T) = (-27.88 \pm 0.34) + 0.5 \ln T - (1500 \pm 150)/T \quad (E')$$

$$\chi^2 = 0.309$$

$$\ln k_1(T) = (-45.31 \pm 1.48) + (2.76 \pm 0.16) \ln T \quad (F)$$

$$\chi^2 = 0.162$$

$$\ln k_1(T) = (-47.55 \pm 7.10) + (3.05 \pm 0.69) \ln T + (204 \pm 4740)/T \quad (G)$$

$$\chi^2 = 0.163$$

$$k_1(T) = (2.48 \pm 1.71) \times 10^{-13} T^{1/2} \exp[(-1032 \pm 410)/T] \\ + (1.41 \pm 0.72) \times 10^{-9} T^{1/2} \exp[(-13989 \pm 1800)/T] \quad (H)$$

$$\chi^2 = 0.08$$

Figure 3 shows a plot of the fitting functions computed compared to the data obtained. Expressions (F) and (G) give essentially identical curves. All of the forms tested, except the double exponential, (H), fail to attain the large value for k_1 observed at 1830 K. Expression (H), which is a convenient form for use in kinetic modeling studies, represents the best fit to the data obtained and is the recommended expression for $k_1(T)$; higher degree polynomials than those given above in expressions (E)-(G) result in oscillations in $k_1(T)$ which cause the fitting expressions to exhibit physically unrealistic local maxima and minima in regions of the 310-1830 K range where no data were obtained. This latter fact, as well as the statistical significance tests applied are reasonable grounds for rejecting polynomials of degree greater than unity.

B. Wall oxidation coefficient

As in the earlier HTFFR measurements, the plots from which the homogeneous rate coefficients are obtained have positive intercepts. In a limited number of experiments the k_{wall} values are less than the calculated diffusion limited values allowing calculation of a wall oxidation coefficient, γ_{Al} .^{2,15} The γ_{Al} thus obtained (and their standard deviations) are in units of 10^{-3} ; 1.9 ± 1.4 [2], 5.8 ± 1.8 [4], 6.2 ± 4.2 [4], 12.7 ± 8.3 [5], and 4.5 ± 4.0 [8] at 310, 480, 730, 1470, and 1830 K, respectively; here the numbers in brackets signify the number of experiments from which γ_{Al} was obtained at each temperature. Within the scatter of these data no definite temperature dependence is evident. Combining all γ_{Al} measurements leads to a value $\gamma_{\text{Al}} = (7.7 \pm 6.8) \times 10^{-3}$, i.e., γ_{Al} can be taken to be in the 1×10^{-3} to 1×10^{-2} range. This γ pertains to oxidation on oxide coated walls on an alumina (470-1830 K) or copper (300 K) substrate. This continuous formation of non-volatile Al oxide coatings on the walls in the course of the experiments is in itself probably the factor responsible for the large scatter in the γ_{Al} measurements, i.e., is responsible for variation in wall reactivity.

C. Accuracy of the $k_1(T)$ measurements

1. Concentrations and time

The uncertainty in k_1 due to inaccuracy in the volume flow rate, pressure and temperature (discussed in Sec. III.C.2) measurements is estimated to be $\pm 20\%$. Additionally, at the flow conditions used, selected to give (i) adequate Al transport and (ii) acceptable temperature accuracy (see Sec. III.C.2), the flow profiles are calculated to be intermediate between plug and parabolic flow. If the former condition had prevailed (the criteria for which have been developed by Walker^{16,17}) η in the expression $t = x/\eta\bar{v}$

would have been 1.0. If the latter had prevailed, for the development of which inadequate distance is available,^{18,19} $\eta = 1.6$. For this reason we have again^{1-3,15} taken $\eta = 1.3 (\pm 0.3 = 23\%)$ for the k_1 calculations.

The question arises whether higher accuracy would be achievable if η were calculated for each individual experiment. However, in the intermediate flow regime of the experiments no analytical solution apparently is possible, nor does it seem likely that a numerical treatment (similar in kind to that of Ref. 18) would be helpful since inspection of Table I shows that the scatter in the k_1 values obtained under nearly identical flow conditions is comparable to that which pertains at widely different conditions. The reasons for this are probably related to the high somewhat variable wall reactivity and the (thin) metal oxide deposits along the reactor walls. In this light, taking a separate error factor of $\pm 23\%$ for η may lead to an overestimate in the combined uncertainty factor, since the same factor must to some degree be reflected in the data scatter. However, it can readily be seen (by estimating the accuracy of k_1 using the usual procedure of taking the square root of the sum of the squares of the individual error estimates)^{1-3, 15} that the contribution of this 23% factor on top of the discussed 20% systematic error and the 25 to 30% standard deviation (cf. Table 1) is minor. (Slight overestimation of errors is probably the most forgivable of sins.)

It is interesting to note that, in flow tube studies of non-refractory species such as O, N, H, or halogen atoms, rate coefficient accuracies in the range of 10-20% are readily obtainable, especially at room temperature (see e.g., Refs. 20-23). The major differences between those studies and the present flow tube work with refractory species are that in the former plug flow conditions are readily obtained ($\eta = 1$ within 5%)^{17,24,25} and γ can be kept

small (on the order of 10^{-5} at 300 K)²⁵ and constant.²⁶ However, some of the temperature inaccuracies discussed below are also present at temperatures other than room temperature in those (and other) kinetic studies, though they often appear to go unrecognized.

2. Temperature

Because of the strong and interesting temperature dependence of k_1 , a careful reexamination of the accuracy of the temperature determinations has been made. Temperature is measured with a Pt/Pt-10% Rh thermocouple (TC), attached to the CO₂ distributor ring⁶ and situated 0.5 cm from the reactor wall. The leads to the TC junction are fed through a two-hole alumina "thermocouple tube" and the junction itself is covered with alumina paste. For the conditions of this work (Mach number ≤ 0.2 ; Reynolds number with respect to the reaction tube diameter ≤ 2300 at 310 K, ≤ 1000 at the other temperatures; Reynolds numbers with respect to the coated thermocouple diameter ≈ 0.13 times those for the reaction tube) radiative heat transfer between the TC junction and the reactor walls is the potential major source of systematic uncertainty.²⁷ As a first step in evaluating the significance of this factor calculations were made of axial and radial temperature distributions for unobstructed laminar flow of Ar in a uniformly heated HTFFR by solving the Graetz equation.^{28,29} The flow conditions used, Table I, are found to satisfy the criteria that the calculated mean gas temperature at the upstream boundary of the reaction zone be within 5% of the nominal wall temperature and that the extremes of radial temperature variation be within 5% of this mean temperature. The actual variations are undoubtedly smaller for the following reasons: (i) laminar, unobstructed flow is assumed in the calculation, whereas the Al source and its support tube (Fig. 1 and Ref. 6) leave

only a small flow path in the source area, which increases thermal contact with the walls, (ii) flow development with reaction time aids the establishment of thermal equilibrium between the gas and walls, and (iii) the simplified model does not take into account the capability of the three heating zones⁶ of Reactor 1 to produce an upstream zone at a higher temperature than the reaction zone, i.e., to allow preheating of the Al/Ar flow. Thus on this basis, the temperature measurement error would be considerably less than 5%. Indeed, measurements were made comparing centerline and offset (to the position used in the experiment) TCs showing that radial temperature gradients are negligible (centerline and offset temperatures agree to $\approx 0.1\%$ of \bar{T}). (Interestingly, when the source tube was removed radial temperature gradients increased to as much as 5% of \bar{T} .)

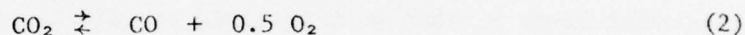
Direct evidence that radiative heating is not causing an overestimate of T is the consistent observation that when the bath Ar flow is turned off at the end of an experiment the indicated reaction zone temperature decreases, which shows that the gas is hotter than the walls. As an additional check, experiments were carried out in which the HTFFR centerline temperatures were obtained simultaneously from two TCs: one similar to those used in the rate coefficient measurements and the other, 5 cm upstream, an identical TC shielded²⁷ by placing it in the center of a 6 cm long, 1.8 cm o.d., 1.2 cm i.d. alumina (open-ended) cylinder. Comparisons were performed for typical experimental conditions near 730 and 1470 K. In all cases the shielded TC tended to indicate slightly higher temperatures, thus some radiative cooling of the TCs used in the rate coefficient measurements occurred. However, in all cases the agreement between the two TCs was within 5% and was best at low pressure (3 Torr) and at 1470 K.

Additionally, for measurements obtained with modular Reactor 2 significant falsification of the TC readings can be ruled out since varying the fraction of bath gas (Ar) which flowed into the reactor through the source, Fig. 1 (temperature near 1700 K) between 1.0 and 0.03 had no apparent effect on the measured k_1 values (the remainder, i.e., the "main gas" entered the reactor at room temperature). Because of the temperature dependence of k_1 some effect of these flow variations would have been observed if the reaction zone temperature had varied significantly. Thus \bar{T} was essentially the same in all the "310 K" measurements and must have been close to this temperature since the gas mixture in the case where 97% of the Ar entered the reactor at room temperature could not have achieved a significantly higher \bar{T} . Similarly, no influence of varying the main to source gas flow ratio on the k_1 measurements with Reactor 3 could be observed.

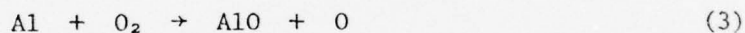
In addition to these considerations indicating systematic errors to be $\leq 5\%$, the precision of the \bar{T} measurements has to be considered. \bar{T} values of the individual experiments of Table I are the averages of the T measurements over the useful length of the reaction zone.¹⁵ The standard deviation, of the T at the various CO₂ inlet positions, from \bar{T} was 2 to 3%. Thus the uncertainty of the T measurements of the individual experiments is $\leq [(5.0)^2 + (2.5)^2]^{1/2} = 5.6\%$. To determine the accuracy of the \bar{T} for the set of experiments at a given nominal temperature, the standard deviation of the set of \bar{T} measurements should be taken into account. Inspection of Table I shows that this factor varies from 1 to 4% and thus contributes only slightly to the cumulative uncertainty; $\leq 6\%$ may be taken as the approximate uncertainty figure for general \bar{T} considerations.

3. The 1830 K rate coefficient measurements

At equilibrium at 1830 K, CO_2 is appreciably dissociated at the partial pressures of interest. We have calculated the effect such dissociation could have had on the k_1 (1830 K) measurements by using an AeroChem thermodynamic equilibrium computer code and JANAF⁴ log K_p data. The principal dissociation products are CO and O_2 , with only minor amounts ($< 0.05 [\text{O}_2]$) of O atoms and no other products (C_2O and C_3O_2 were considered) present. Because of its strong bond ($D(\text{C-O}) \approx 260 \text{ kcal mole}^{-1}$) CO could react with Al only in a three-body process, of which there is no evidence in the data ($k_1(1830 \text{ K})$ does not increase with P). However the O_2 from the equilibrium



will react with Al. For the reaction



we previously determined^{1,2} (in the same apparatus) a rate coefficient of $(3.4 \pm 2.2) \times 10^{-11} \text{ ml molecule}^{-1} \text{ s}^{-1}$. Thus if CO_2 would have been completely dissociated, an apparent $k_1 = 0.5 k_3$ would have been observed, lower than the actual k_1 measurements. The calculated fractional equilibrium dissociation $\alpha = 1 - [\text{CO}_2]/[\text{CO}_2]_0$ (where $[\text{CO}_2]_0$ is the $[\text{CO}_2]$ before dissociation or reaction) varies over the range of $[\text{CO}_2]_0$ used in the experiments, from 0.57 at $[\text{CO}_2]_0 = 1 \times 10^{12} \text{ ml}^{-1}$ to 0.07 at $[\text{CO}_2]_0 = 1 \times 10^{15} \text{ ml}^{-1}$. Using these numbers the actual observations were then "corrected" by obtaining k_1 values from plots of the following equations (compare Ref. 2):

$$\text{Stationary: } -\ln[\text{Al}]_{\text{rel}}^{\text{corr}} = -\ln[\text{Al}]_{\text{rel}}^{\text{obs}} - k_3[\text{O}_2]t = k_1[\text{CO}_2]t + k_{\text{wall}}t$$

$$\text{Traversing: } k_{\text{ps}_1}^{\text{corr}} = k_{\text{ps}_1}^{\text{obs}} - k_3[\text{O}_2] = k_1[\text{CO}_2] + k_{\text{wall}}$$

The mean of the k_1 thus obtained was found to be 6% higher than that of Table I. Thus while CO_2 dissociation could contribute somewhat to the uncertainty in $k_1(1830 \text{ K})$ this effect appears minor compared to the standard deviation (Table I) and error factors already discussed (Sec. III.C.1). There is moreover no evidence that equilibrium dissociation was achieved. Such is in fact unlikely on the basis of the observations that (i) there are no trends in the individual $[\text{Al}]_{\text{rel}}$ (or k_{ps_1}) plots versus CO_2 which indicate consistent deviations from linearity and (ii) a few stationary inlet measurements made at a measured T of $\approx 1900 \text{ K}$ (representing the approximate maximum safe operating temperature of the HTFFR) indicated a somewhat lower k_1 than that obtained at 1830 K, which moreover decreased with increasing reaction time, indicative of CO_2 dissociation at that temperature and negligible dissociation at 1830 K.

4. Recommended k_1 values

For k_1 at each of the five nominal temperatures of Table I the uncertainty can now be obtained by taking the square root of the sum of the squares of the individual error assessments, which thus consist of the standard deviations and the 20% and 23% factors of Sec. III.C.1. Taking the temperature accuracy as $\pm 6\%$, cf. Sec. III.C.2, we thus obtain from Table I:

$$k_1(310 \pm 20 \text{ K}) = (1.5 \pm 0.6) \times 10^{-13} \text{ ml molecule}^{-1} \text{ s}^{-1}$$

$$k_1(480 \pm 30 \text{ K}) = (6.9 \pm 2.7) \times 10^{-13} \text{ ml molecule}^{-1} \text{ s}^{-1}$$

$$k_1(730 \pm 40 \text{ K}) = (1.6 \pm 0.7) \times 10^{-12} \text{ ml molecule}^{-1} \text{ s}^{-1}$$

$$k_1(1470 \pm 90 \text{ K}) = (9.0 \pm 3.8) \times 10^{-12} \text{ ml molecule}^{-1} \text{ s}^{-1}$$

$$k_1(1830 \pm 110 \text{ K}) = (3.8 \pm 1.5) \times 10^{-11} \text{ ml molecule}^{-1} \text{ s}^{-1}$$

To obtain k_1 at any other temperature, Equation (H) of Sec. III. A should be used to obtain the mean value and experimental error. The accuracy can then

be obtained by combining this error with the 20% and 23% factors, as above.

D. The lower limit to $D(\text{Al-O})$

While Reaction (1) has a strongly curved Arrhenius plot, Figs. 2 and 3 show that, over the 310 to 730 K range, $k_1(T)$ adheres quite well to Arrhenius behavior with an activation energy $E_{\text{act}}(1) = 2.6 \pm 1.3 \text{ kcal mole}^{-1}$; these error limits reflect the discussed precision and possible systematic inaccuracy sources in both k_1 and T . Since $\Delta H(1) \leq E_{\text{act}}(1)$, Reaction (1) can at most be 3.9 kcal endothermic; if the classical $T^{0.5}$ factor in the pre-exponential had been included in the calculation (which procedure may not be justifiable in view of e.g., the T^0 -dependence of the rate coefficients of the Al/O_2 and AlO/O_2 reactions)¹ an even smaller endothermicity would have resulted. Using JANAF ΔH (individual species) values⁴ a $\Delta H(1)$ of 6.0 and 5.8 kcal mole⁻¹ is calculated at 300 and 800 K, respectively. The JANAF data are based on $D(\text{Al-O}) = 120 \pm 2 \text{ kcal mole}^{-1}$ and only this upper limit would thus be within the range allowed by the measured $E_{\text{act}}(1)$ values. Since endothermic reactions usually have an activation energy at least somewhat higher than their ΔH this finding thus casts some doubt on the JANAF $D(\text{Al-O})$ value. Dagdigian, Cruse and Zare⁵ have recently determined a lower limit to $D(\text{Al-O})$ and combining their value with an evaluation of the literature for the upper limit, they recommend $D(\text{Al-O}) = 121.5 \pm 1 \text{ kcal mole}^{-1}$, accepting essentially the same upper limit as JANAF. However, improved laser fluorescence experiments by Dagdigian and Pasternack,³⁰ now in progress, using a velocity selected Al beam³¹ lead them to recommend $D(\text{Al-O}) = 123.0 \pm 1 \text{ kcal mole}^{-1}$. Flame photometric data, notably Ref. 32, also tend to indicate higher $D(\text{Al-O})$ values. Those determinations are dependent on the f -number of the AlO(B-X) transition, which has been determined accurately in the same work of Dagdigian, Cruse and Zare.⁵ Using this f number the

data of Ref. 32 reduce³³ to $D(\text{Al-O}) = 132 \pm 6 \text{ kcal mole}^{-1}$. On the basis of all these data we conclude that $D(\text{Al-O})$, and hence ΔH of Reaction (1), may not yet be accurately known and consider it probable that $D(\text{Al-O})$ is a few kcal mole^{-1} larger than 122. We are presently measuring the activation energy of a reaction of Al with an oxidizer having an O atom more strongly bonded than in O-CO, i.e., O-SO, in an attempt to help clarify this problem.

IV. DISCUSSION

The present work represents the first time that a reaction having a definite activation energy has been measured from near room temperature to a "high" temperature such as 1800 K, by a single technique. Over such a wide T-range some deviation from Arrhenius behavior may be anticipated, since the simplifying approximations on which the Arrhenius law is based become quite inaccurate.^{34,35} Such deviation can be especially strong for reactions having low activation energies, such as Reaction (1) where the temperature-dependence of the entropy of activation can become the dominating factor in the k_1 -T dependence. The strong deviation from Arrhenius behavior here observed thus is remarkable but certainly not unprecedented; for example, some reactions of OH^{20,36-38} and O³⁹ show somewhat similar behavior and have been thoroughly discussed. In fact,⁴⁰ in the sense that Al may be considered an H substitute, Reaction (1) is the reverse of what is now a classical case of such behavior, viz. the reaction $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$.^{20,36,38,41}

Transition state theory (TST) probably offers the most general promise to describe non-Arrhenius behavior. However, as in the case of the Al/O₂ and AlO/O₂ reactions,¹ TST is of little predictive help at present for simple metathesis reactions of metallic species. Figure 3 shows that the best fit to a TST form (curve G) is inadequate to describe the high

temperature behavior of k_1 . It is certainly possible to a posteriori assemble a set of assumptions to rationalize the $T^{2.5}$ dependence of k_1 indicated by the curve G equation (Sec. III.A). From TST the pre-exponentials A for the linear and bent intermediate complexes are:

$$A \text{ (linear)} = C_\ell T^{-0.5} \prod_{i=1}^6 \left(1 - \exp(-h\nu_i^\ddagger/kT)\right)^{-1} / \prod_{i=1}^4 \left(1 - \exp(-h\nu_i^{CO_2}/kT)\right)$$

$$A \text{ (bent)} = C_b \prod_{i=1}^5 \left(1 - \exp(h\nu_i^\ddagger/kT)\right)^{-1} / \prod_{i=1}^4 \left(1 - \exp(-h\nu_i^{CO_2}/kT)\right)^{-1}$$

where C_ℓ and C_b are the lumped, temperature-independent constants arising from translational, rotational, and vibrational partition functions of the reactants and the transition state. At 1830 K only the ν_2 mode of CO_2 is in the high temperature limit ($h\nu_2 \ll kT$) under which condition $A \text{ (linear)} \propto T^{2.5}$ and $A \text{ (bent)} \propto T^2$ if the transition state vibrations were also at their high temperature limits. However, it appears likely that this state will have high energy stretching modes that do not fulfill the $h\nu_i^\ddagger \ll kT$ condition at this temperature which would result in a decreased T-dependence. Since no information is available on the vibrational levels of the postulated intermediates further speculation does not appear productive. As Benson^{42, 43} has pointed out activation energies for metathesis reactions are not yet well understood and a large experimental data base on sets of similar reactions is required to predict activation energies from TST-based empiricism. For metal oxidation reactions such a data base is not yet available; the present work and that of Ref. 1 hopefully represent one of the first pieces of information from which it may eventually be constructed.

Thus additional factors need be considered to "explain" the observed k_1 -T behavior. Expression (H) of Sec. III.A and Fig. 3, which gives the best fit to the data, is the type of expression which arises from complex processes, e.g., the opening of a second product channel at high temperature, or the increased participation of excited reagent states as the population of these states increases with T. The first term of Equation (H) describes the discussed (Sec. III.D) low temperature Arrhenius behavior quite well; however, the pre-exponential of the second term is unrealistically high and suggests that this term is useful merely as a curve-fitting expression and appears to result from more than one such additional process participating at high temperature.

A possible second product channel would be the formation of $AlO(A^2\Pi)$, which lies⁴⁴ 15.1 kcal mole⁻¹ above $AlO(X^2\Sigma)$ and thus would require an activation energy ≥ 15.1 kcal mole⁻¹, cf. Equation (H). With regard to increased participation of excited reagent states, it is now well established that vibrational excitation can lead to major increases in rate coefficients and make additional reaction channels accessible, e.g. Refs. 45, 46. Menzinger et al^{47,48} have shown that cross sections of some metal atom/ N_2O reactions are enhanced by vibrational excitation of N_2O and have made it plausible that the bending mode ν_2 is responsible for these observations. Their^{47,48} postulated mechanism is initial electron transfer from the metal atom to N_2O forming an ion pair, i.e., a harpooning type mechanism, which processes often have high (on the order of 3×10^{-9})⁴⁹ pre-exponentials. Since ground state linear N_2O has a negative electron affinity but this affinity increases as the molecule is bent (N_2O^- has a bent ground state), the observed cross section increases with [N_2O , $\nu = 2$]. For the iso-electronic species CO_2

which has similar configurations for the neutral and negative ion ground states,⁵⁰ increased $[\text{CO}_2, \nu = 2]$ could similarly increase the observed k_1 . In fact, while formation of CO_2^- by electron attachment to ground state CO_2 is prevented by the difference in structure, the work of Cooper and Compton⁵¹ on gas phase reactions between Cs atoms and organic molecules containing bent CO_2 supplies evidence for the ready formation of CO_2^- in reactions involving such CO_2 . The total population of CO_2 bent states can be shown, using data from Herzberg,⁵² to increase by a factor of 10 over the 310 to 1830 K. Thus it appears likely that excitation of specific vibrational states of CO_2 can contribute to the rapid increase in k_1 , but this factor cannot quantitatively be evaluated in the absence of information on the reactivity of CO_2 in such states. Finally, excited electronic states of Al are not significantly populated at the temperatures covered in this work, while the two low-lying spin-orbit states $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ are both significantly populated at all temperatures covered (at 300 K Al vapor is 45.4% $^2\text{P}_{1/2}$ and 53.6% $^2\text{P}_{3/2}$ while at 1800 K Al is 35.1% $^2\text{P}_{1/2}$ and 64.9% $^2\text{P}_{3/2}$) so that no major effect on the reaction rate can arise from them.

V. CONCLUSIONS

One of the major objectives in the development of the HTFFR technique was to allow kinetic measurements from near 300 K to near 2000 K by a single experimental technique, thereby overlapping the temperature domain of traditional near room temperature techniques with that of traditional high temperature techniques such as flames and shock tubes. The present work represents the first time that this objective has been attained for a reaction having a definite activation energy. Over the low temperature (310-730 K) part of the $\ln k_1$ vs. T^{-1} plot Arrhenius behavior is found to be followed. The

activation energy derived from this straight part of the plot (≤ 4 kcal mole⁻¹) has been shown (Sec. III.D) to be only barely compatible with the upper limit (122 kcal mole⁻¹) to D(Al-O) often assumed. At $T > 730$ K, k_1 is found to increase much more rapidly than the Arrhenius law would indicate; this is probably (Sec. IV) due to a combination of factors including, in addition to the entropy of activation factor inherent in transition state considerations, the likely participation of a second reaction channel leading to AlO(A²Π) and/or preferential reaction of Al with CO₂ in bending modes. A definitive quantitative explanation of the T-dependence of k_1 could probably only be made if state-to-state experiments on the Al/CO₂ reaction at the right interaction energies were available. Since k_1 cannot reasonably be expected to rise by more than an order of magnitude with further increases in T, it would be interesting to see an extension of the present measurements to even higher temperatures (under conditions where [CO₂] is accurately known) by traditional high temperature techniques. The overlapping temperatures for such work provided here can be used as check points for those measurements.

ACKNOWLEDGMENTS

We thank J.J. Houghton, R.L. Revolinski, and R. Ellison for capably carrying out the experimental work, W.R. Frenchu for computational assistance, Dr. W.J. Miller (AeroChem), Dr. N.M. Laurendeau (Purdue University), Dr. D.E. Rosner (Yale University), and Dr. R.N. Zare (Columbia University) for helpful discussions, and Dr. D.E. Jensen (Rocket Propulsion Establishment, Westcott, England) and Dr. P.J. Dagdigian (Johns Hopkins University) for sending us material prior to its publication.

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TABLE I. Summary of $\text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO}$ measurements

Mode ^a	P (Torr) ^b	\bar{v} (m s ⁻¹)	$[\text{Al}]_i$ (% abs.) ^c	$[\text{CO}_2]$ (10 ¹⁵ ml ⁻¹)	\bar{T} (K)	k_1 (10 ⁻¹³ ml molecule ⁻¹ s ⁻¹)
Reactor 2, 310 K nominal						
TF309.3	3.0	10	6	0.25 - 1.0	300	2.0
TF309.3	3.3	27	18	1.6 - 4.6	310	1.3
TF309.3	3.5	44	20	2.5 - 7.8	320	2.0
TF309.3	10	11	14	0.18 - 1.9	300	1.6
TF309.3	11	29	4	1.0 - 3.2	310	1.4
TF309.3	11	47	13	1.1 - 5.0	310	1.6
TF309.3	20	10	4	0.9 - 1.6	310	1.8
TF309.3	21	29	4	0.8 - 6.1	310	1.0
TF309.3	21	48	11	0.7 - 6.4	320	1.1
Avg. ^d					310 ± 10	1.5 ± 0.4

				$[\text{CO}_2]$ (10 ¹⁴ ml ⁻¹)	k_1 (10 ⁻¹³ ml molecule ⁻¹ s ⁻¹)	
Reactor 3, 480 K nominal						
TF309.3	3.1	19	5	2.2 - 14	480	5.3
TF309.3	3.1	21	18	3.6 - 15	480	6.9
TF309.3	3.2	47	4	3.2 - 15	480	6.8
TF309.3	3.2	48	15	2.0 - 10	480	10.2
TA309.3	5.8	48		2.0 - 12	490	9.9
TF309.3	10	11	6	3.7 - 9.0 ^e	460	5.2
TF309.3	10	21	20	0.8 - 4.1 ^e	480	6.6
TF309.3	11	53	6	3.9 - 14	460	6.1
TA309.3	17	22		1.3 - 26	490	6.0
TF309.3	20	11	8	2.0 - 7.0	490	6.8
TF309.3	20	21	18	4.6 - 11	470	5.1
TF309.3	21	43	16	4.7 - 10	460	7.7
Avg. ^d					480 ± 10	6.9 ± 1.7

TABLE I (Continued)

Mode ^a	P (Torr) ^b	\bar{v} (m s ⁻¹)	[Al] _i (% abs.) ^c	[CO ₂] (10 ¹⁴ ml ⁻¹)	\bar{T} (K)	k_1 (10 ⁻¹² ml molecule ⁻¹ s ⁻¹)
Reactor 1 (except as noted by f), 730 K nominal						
TF309.3 ^f	3.8	32	3	1.9 - 10	720	1.4
TF309.3	4.3	56	5	1.0 - 6.6	800	1.9
SF309.3	3.8	78	6	0.5 - 22	710	1.9
TF309.3	3.8	80	6	0.5 - 12	720	1.5
TF309.3	11	20	3	0.5 - 2.0	780	1.8
TA309.3 ^f	10	42		2.9 - 18	710	0.8
SF309.3	11	52	4	0.1 - 7.2	730	2.2
SF309.3	11	98	3	0.6 - 21	710	1.3
SA309.3	11	101		0.5 - 19	740	1.6
TA309.3 ^f	19	20		0.6 - 3.3	730	2.6
SA309.3	22	35		0.1 - 10	740	1.3
SF309.3	29	25	4	0.1 - 6.8	710	1.5
TF309.3	30	52	5	2.0 - 9.0	720	1.4
				Avg. ^d	730 ± 30	1.6 ± 0.5

TABLE I (Continued)

Mode ^a	P (Torr) ^b	\bar{v} (m s ⁻¹)	[Al] _i (% abs.) ^c	[CO ₂] (10 ¹³ ml ⁻¹)	\bar{T} (K)	k ₁ (10 ⁻¹² ml molecule ⁻¹ s ⁻¹)
<u>Reactor 1, 1470 K nominal</u>						
TA309.3	3.2	26		8.3 - 16 ^e	1430	8.1
SA396.2	3.5	43		2.4 - 11	1480	11
TA396.2	3.5	49		11 - 41	1470	9.6
TA309.3	3.4	88		8.2 - 28	1470	8.8
TA309.3	8.6	26		2.3 - 11	1480	7.8
SA396.2	8.6	49		1.1 - 23	1500	9.1
SF309.2	8.6	93	9	3.8 - 65	1450	4.4
SA396.2	8.6	95		4.6 - 72	1500	5.4
TA309.3	16	25		3.8 - 15	1480	6.3
SA309.3	16	25		0.4 - 26 ^e	1480	7.3
SA396.2	16	48		1.3 - 24 ^e	1430	12
SA396.2	16	97		1.7 - 47	1440	11
SF309.3	16	99	5	1.8 - 15	1460	8.5
TA396.2	31	50		4.0 - 45 ^e	1430	7.2
SA396.2	31	50		1.5 - 38	1450	14
TA396.2	31	51		4.7 - 19	1470	11
SA396.2	31	52		1.7 - 16	1500	14
SF309.3	32	100	5	1.7 - 10	1460	6.5
				Avg. ^d	1470 ± 20	9.0 ± 2.7

TABLE I (continued)

Mode ^a	P (Torr) ^b	\bar{v} (m s ⁻¹)	[Al] _i (% abs.) ^c	[CO ₂] (10 ¹² ml ⁻¹)	\bar{T} (K)	k ₁ (10 ⁻¹¹ ml molecule ⁻¹ s ⁻¹)
<u>Reactor 1, 1830 K nominal</u>						
SA309.3	4.1	93		8.0 - 122	1850	3.6
SA394.4	12	10		1.4 - 12 ^e	1840	6.2
SA309.3	13	15		2.5 - 21 ^e	1840	2.7
SA394.4	12	25		1.6 - 34 ^e	1810	3.8
SA394.4	14	90		1.0 - 570	1830	3.5
SA394.4	30	10		1.3 - 8.1	1830	3.5
TA394.4	30	10		4.7 - 13 ^e	1820	5.5
SA309.3	31	14		2.3 - 34 ^e	1820	3.2
SA394.4	31	25		1.0 - 14 ^e	1820	2.4
SA309.3	32	47		3.5 - 56 ^e	1830	3.4
				Avg. ^d	1830 ± 10	3.8 ± 1.2

a The first letter, T or S, indicates whether the CO₂ inlet nozzle was traversed or kept stationary; the second letter F or A, whether [Al]_{rel} was measured in fluorescence or absorption; the number indicates the wavelength (in nm) of the Al line used.

b 1 Torr = 133.3 Pa

c % initial Al absorption is shown for the experiments in which [Al]_{rel} was monitored by fluorescence; for the 310 and 1470 K experiments the 396.3 nm line was used for this absorption measurement while in the 480 and 730 K work the 309.3 nm line was used. In experiments in which [Al]_{rel} was obtained by absorption the initial absorption was on the order of 50%.

d Mean and standard deviation

e In these experiments 9.56% CO₂ in Ar was used, in all other experiments undiluted CO₂.

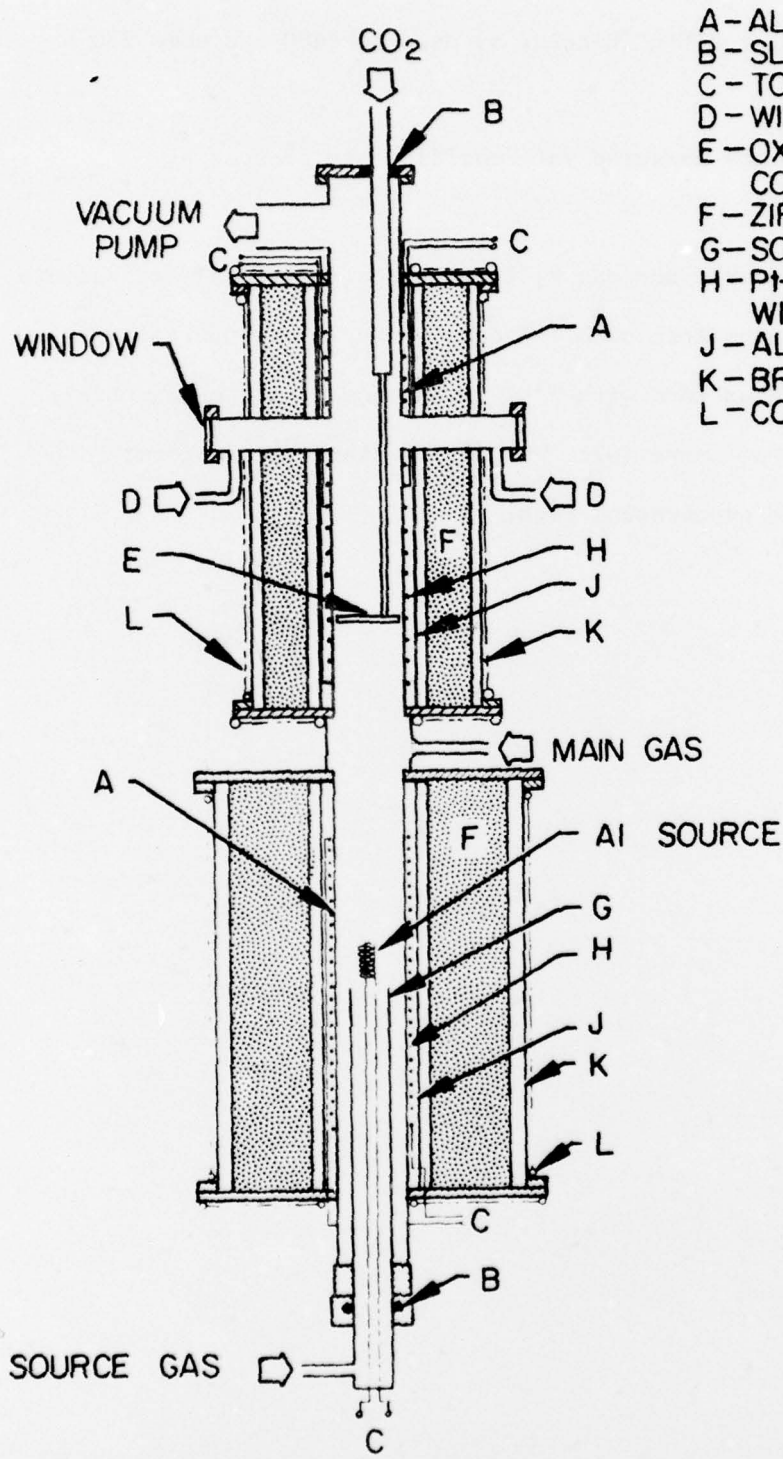
f These experiments were carried out in Reactor 3.

FIGURE CAPTIONS

FIG. 1 Schematic of modular HTFFR (Reactor 3) used for 480 and some 730 K experiments

FIG. 2 Arrhenius plot of the measured rate coefficients grouped by temperature.

FIG. 3 Comparison of fitting functions $k_1(T)$ with the individual data points
Curve (E): Arrhenius form with T-independent pre-exponential;
Curve (E'): Arrhenius form with $T^{1/2}$ dependence of pre-exponential;
Curve (F): T^n form; Curve (G): Transition state theory form;
Curve (H): Double exponential form.



- A-ALUMINA TUBE
- B-SLIDING O-RING SEAL
- C-TO POWER SUPPLY
- D-WINDOW SWEEPER GAS
- E-OXIDANT INLET and THERMO-
COUPLE WELL
- F-ZIRCAR INSULATION
- G-SOURCE HOLDER
- H-Pt-40% Rh RESISTANCE
WIRE
- J-ALUMINA HEAT SHIELD
- K-BRASS VACUUM HOUSING
- L-COOLING COIL

FIG. 1

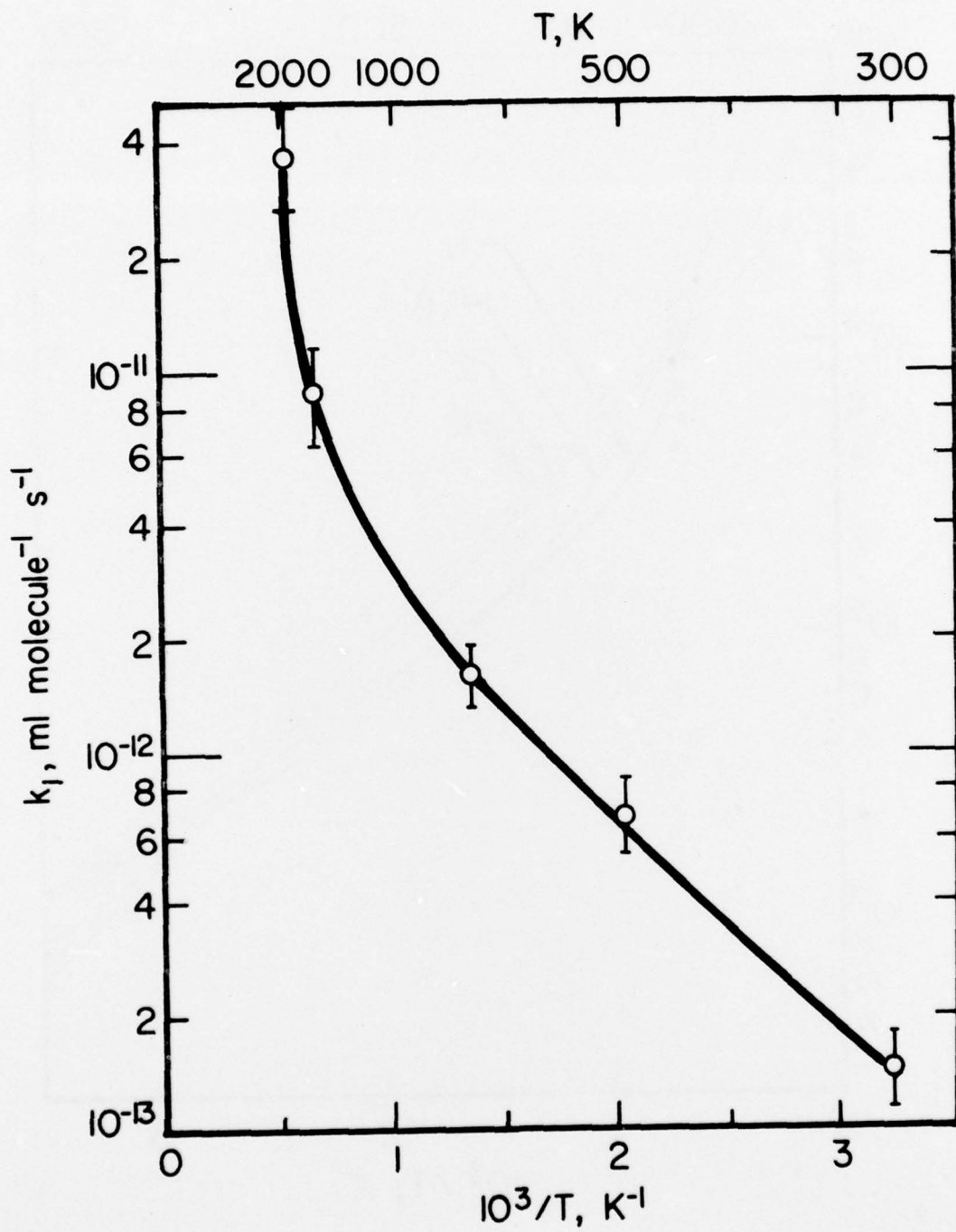


FIG. 2

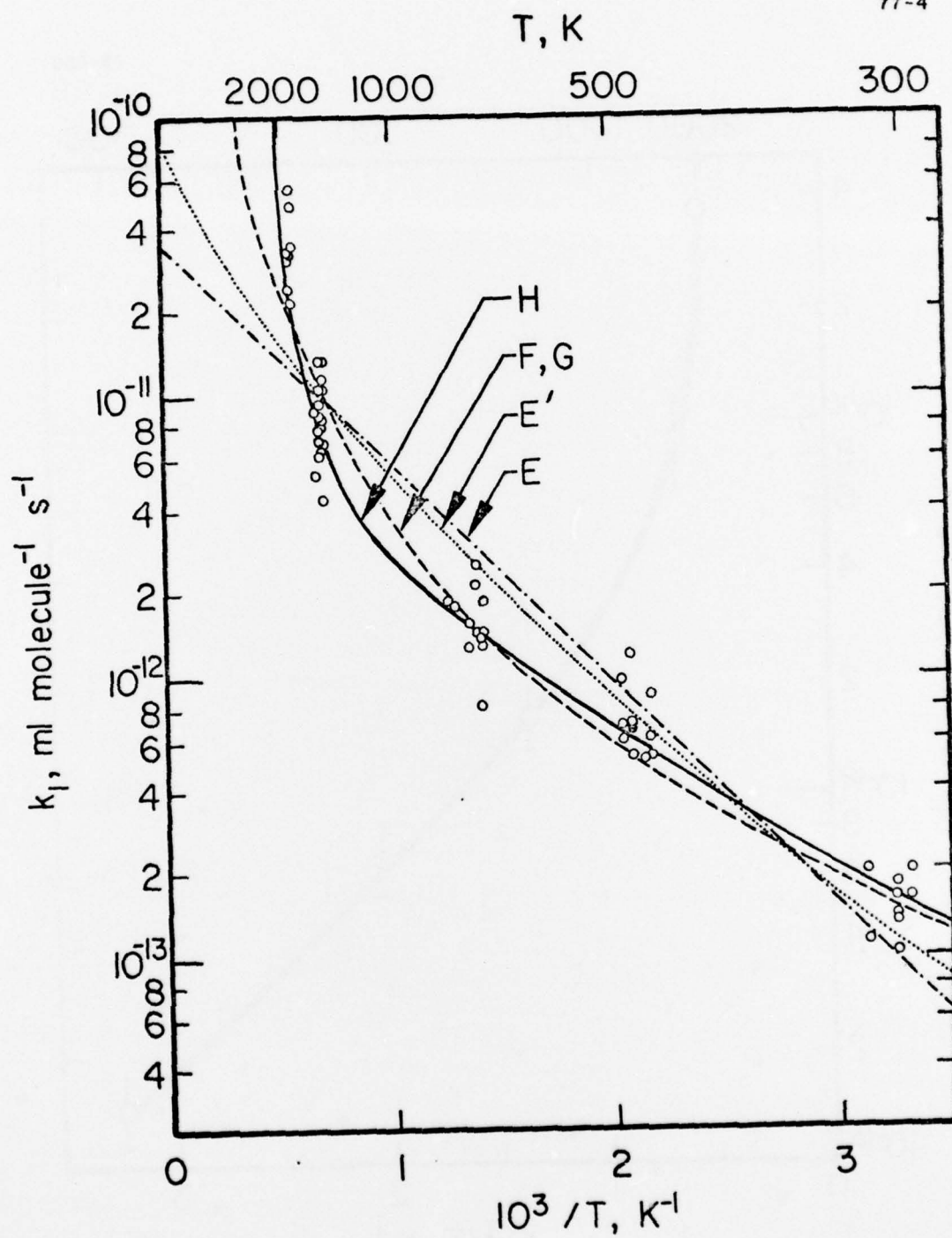


FIG. 3

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) HTFFR KINETICS STUDIES OF $\text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO}$ FROM 300 to 1800 K, A NON-ARRHENIUS REACTION ✓		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER AeroChem TP-353 ✓
7. AUTHOR(s) Arthur Fontijn William Felder		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS AeroChem Research Laboratories, Inc. P.O. Box 12 Princeton, NJ 08540 ✓		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE March 1977 ✓
		13. NUMBER OF PAGES 44
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Reaction Kinetics Combustion Al (metal atoms) CO ₂		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) High-temperature fast-flow reactors (HTFFR) were used to obtain the rate coefficients, k_1 (and their accuracies), for the reaction $\text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO}$. At 310, 480, 730, 1470, and 1830 K, k_1 is found to be $(1.5 \pm 0.6) \times 10^{-13}$, $(6.9 \pm 2.7) \times 10^{-13}$, $(1.6 \pm 0.7) \times 10^{-12}$, $(9.0 \pm 3.8) \times 10^{-12}$ and $(3.8 \pm 1.5) \times 10^{-11}$, respectively (all in $\text{ml molecule}^{-1} \text{ s}^{-1}$ units). For this temperature range $k_1(T)$ may be expressed by the curve fitting equation $k_1(T) = 2.5 \times 10^{-13} T^{1/2} \exp(-1030/T) + 1.4 \times 10^{-9} T^{1/2} \exp(-14,000/T)$		

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The data also indicate a wall-oxidation process of zeroth order in $[\text{CO}_2]$ with a γ_{Al} of 10^{-3} to 10^{-2} , not measurably dependent on T. Factors affecting the accuracy of the measurements are discussed. Over the 310-730 K range $k_1(T)$ obeys an Arrhenius expression, with an activation energy of 2.6 ± 1.3 kcal mole $^{-1}$, which implies $D(\text{Al-O}) \geq 122$ kcal mole $^{-1}$. Above 730 K, $k_1(T)$ increases much more rapidly with T. This behavior cannot be described on the basis of simple transition state theory alone; the most probable additional factors involved are the opening of a second reaction channel leading to $\text{AlO}(\text{A}^2\Pi)$ and preferential reaction of Al with CO_2 in bending modes.

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